ORGANIC CHEMISTRY

THE FATTY COMPOUNDS

WHITELEY

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ORGANIC CHEMISTRY

THE FATTY COMPOUNDS

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PREFACE

As it is quite impossible to learn organic chemistry properly by reading only, it has been my endeavour in this work, not only to give students an intelligible and connected account of the theory of the subject, but also to provide them with such information as shall enable them to gain a practical acquaintance with it.

In furtherance of these aims, cross-references have been copiously inserted; processes for the preparation of a large number of compounds have been given, with short (but, it is hoped, sufficient) working detail; and those most suitable for students' work are distinguished by a dagger (†). The principal tests for the best-known compounds are also supplied; and, finally, numerous illustrations have been introduced.

Amongst the many works referred to during the preparation of this volume, the following have been freely employed: Watts' "Dictionary of Chemistry," Thorpe's "Dictionary of Applied Chemistry," Roscoe and Schorlemmer's "Treatise on Chemistry," and Richter's "Organic Chemistry."

I am indebted to Messrs. Matthews and Lott for permission to copy Figures 33, 40, and 44 from their work on "The Microscope in the Brewery;" and to Mr. G. S. Newth for Figures 24, 26, 27, and 28, which are taken from his "Chemical Lecture Experiments."

The starches (Fig. 45) were kindly drawn for me by Mr. E. A. Smith, demonstrator of biology in University College, Nottingham.

Many of the remaining figures are from the above-mentioned dictionaries, by permission of the publishers, while about half of the total number are from photographs of apparatus, which were prepared for me by Mr. J. B. Pursglove.

My hearty thanks are due to my late colleagues, Messrs. J. B. Coleman, A.R.C.Sc., and M. E. Feilmann, B.Sc., for many suggestions, and to them and to Mr. John Allport, M.A., of Richmond, for reading through the proofs.

R. L. W.

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ORGANIC CHEMISTRY

SECTION I.

INTRODUCTORY SUBJECTS.

CHAPTER I.

INTRODUCTION.

THE science of organic chemistry is of comparatively recent growth; for although much practically useful knowledge was shown in the manufacture of vinegar and of the acetates, of soap and of various fermented liquors, neither the labours of the alchemists, nor those of the medical chemists who followed them, did much to increase our knowledge of the chemistry of organic substances.

It is true that during their times a number of substances were isolated and chemical processes were improved, but it was only about the end of the seventeenth century that the function of chemistry was more fully understood, and that Lémery first separated the study of the science into the three branches of mineral, vegetable, and animal chemistry.

Scheele, however, in the latter part of the eighteenth century, was the great pioneer in organic research. Amongst other things he discovered oxalic acid, and distinguished as distinct substances citric, tartaric, and malic acids. Lavoisier about the same time recognised that both animal and vegetable products contain carbon, hydrogen, and oxygen, and more rarely nitrogen and phosphorus; but the term "organic chemistry" was not originated by him, although the division of the science into the two branches inorganic and organic chemistry was consequent upon his labours and those of his contemporaries. It was about 1815 that Berzelius first perceived that organic, as well as inorganic substances, had constant compositions, and he explained the difference between the two classes of compounds by saying that the organic compounds were oxides of *compound radicles*.[1] He, however, still believed that organic bodies could not, like inorganic compounds, be artificially produced; that is, that they could only result from the action of vital processes in plants or animals.

This belief received its deathblow in 1828, when the German chemist Wöhler prepared *urea* synthetically. It had hitherto been supposed unquestionable that urea could only be obtained from urine; yet Wöhler found that when a solution of ammonium cyanate, which can be readily prepared from inorganic sources, was evaporated to dryness, it yielded that substance. In consequence of this result, it became necessary to believe that organic substances, like inorganic, could be produced by artificial means. Some time elapsed before other discoveries were made which confirmed this opinion, but we are now quite released from the trammels of the old ideas, and fully realise that identical laws govern the formation of both inorganic and organic compounds.

Notwithstanding this, it is usual, for purposes of study, to separate what is still termed organic from inorganic chemistry. The main reason for this lies in the specific properties of the carbon atom itself. It stands alone amongst the elements in its extraordinary power of combination, not only with other elements, but also with itself. Its atoms can unite with each other, to an almost infinite extent, to form more or less complex open and closed chains, in which some of its affinities remain free to combine with other elements. There is, indeed, no theoretical limit to the number of such compounds which are producible. The great number of its possible combinations, therefore, renders it convenient to consider the compounds of carbon apart from those of other elements.

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[1] By a compound radicle is meant a group of atoms which occurs in a series of compounds, and which can be replaced as a whole by other radicles or by elements.

Organic chemistry is therefore the chemistry of the carbon compounds, or (as carbon dioxide and disulphide, and the carbonates are generally studied in inorganic chemistry) it might be even better defined as the *chemistry of the hydrocarbons and their derivatives.*

Having now realised why it is advisable to divide the study of chemistry into two main branches, the characteristics of that which deals with organic chemistry may now be more fully discussed, certain preliminary and general subjects being first considered in order, as below—

1. The general sources of organic compounds.
2. Methods employed for obtaining such substances in a pure state.
3. Methods used for the determination of the purity of compounds.
4. Principles of elementary analysis.
5. Calculation of empirical formulæ.
6. Processes employed in the determination of molecular weights.
7. Structure of organic compounds.

CHAPTER II.

SOURCES AND PURIFICATION OF ORGANIC BODIES.

SOURCES OF ORGANIC COMPOUNDS.

ORGANIC compounds are obtained from *four* principal sources. **Firstly,** many are produced as the direct result of vital action, and may generally be prepared from the animal or vegetable substances containing them; *e.g.* urea, the alkaloids, whether of animal or vegetable origin, and the sugars.

Secondly, others are found in naturally occurring substances, which are decomposition products of animal, vegetable, or other materials, *e.g.* ozokerit, hatchettine, fossil-wax, and crude petroleum yield many of the paraffinoid and benzenoid hydrocarbons.

Thirdly, many organic compounds are produced as the result of the destructive distillation of other organic substances. Thus from coal-tar, benzene, naphthalene, carbolic acid, and other materials too numerous to mention, have been isolated. The distillation of wood, too, yields wood spirit (methyl alcohol), acetone, and acetic acid; while that of bones produces many nitrogenous and other substances.

Lastly, a vast number of compounds are prepared in the laboratory by directly synthetical processes; for these, however, it must be remembered that some of the substances in the above-mentioned groups usually form the starting-points.

PURIFICATION OF COMPOUNDS.

It is seldom possible to prepare a compound at once in a state of purity. As a rule it is more or less contaminated with other substances, and has to undergo some special treatment before it is sufficiently pure to be analysed for the determination of its percentage composition.

The methods of purification principally employed are the following :—

1. **Recrystallisation.**—This process is employed when a crystallisable substance is found associated with some other material, either not so readily crystallisable as it; or which is more soluble in some particular solvent. In this case, a solution is made of the material in question, from which on cooling or, if necessary, after concentration, the more readily crystallisable and less soluble body separates out, leaving the impurities in solution. The crystals are collected on a filter, washed with a little of the solvent, and dried. If still not pure (see p. 9), they are recrystallised till the requisite purity is obtained. Thus, in the manufacture of ordinary sugar, the purified juice is concentrated, and on cooling the sugar separates as crystals from the coloured mother liquor. If the crystals are redissolved and the concentration repeated, the sugar will be obtained in a still purer form. Of course, with an unknown substance it will be necessary to experimentally determine the most suitable solvent to employ. In organic

investigations, water, alcohol, ether, chloroform, and acetone, amongst other bodies, find frequent employment.

2. **Separation by Solvents.**—In many cases two substances may be separated from each other by employing solvents in which one of the substances only is soluble. Thus if some dried soap is treated with petroleum ether, that solvent will dissolve out from it any unsaponified oil which remains, and leave the soap itself behind. Similarly, if several substances are in solution together, it is frequently possible to add an immiscible solvent, which on shaking up will abstract a dissolved substance from the first solvent, and as the solutions then form two layers of liquid more or less readily, they can be separated by means of the separating funnel (Fig. 1). This apparatus permits the more dense liquid to be drawn away first, and the dissolved substance is then recovered by distilling off the solvent, or by other means as required.

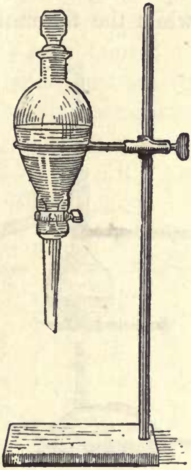
FIG. 1.

3. **Fractional Distillation**, both in its simpler as well as in its more complex form, is of very great service in purifying organic substances. As an example of its simpler use may be instanced the purification of ethylene glycol (p. 218), in which the crude product is simply distilled from an ordinary distillation flask, which is provided with a thermometer connected with a Liebig's condenser (see Fig. 2). The portion of the glycol which distils over while the thermometer rises from 185° to 205° C. is collected apart. That distillate is redistilled, and the fraction collected between 195° and 200° is nearly pure glycol.

There are many cases, however, in which it is impossible, by so simple a process of distillation, to separate liquids from each other by difference of their boiling points; *e.g.* water boils at 100°, alcohol at 78°, yet when a mixture of the two substances is distilled, the distillate is always a mixture.

This difficulty of separation depends upon the different solubilities of the compounds in each other, their varying vapour pressures, etc.; but the laws governing the influence of these conditions are too complex to be discussed in any elementary work.[1]

In such cases the apparatus employed may be the same as that just described, but the manner of operation differs. The mixture of substances to be separated is placed in the flask, which is then heated, and the temperature at which the liquid begins to distil is noted. It is allowed to go on distilling while the thermometer rises through an interval of three or five degrees, when the receiver is changed; that "fraction" coming over during the next similar interval is also collected apart, and the receiver again changed; and so on till the whole, or nearly the whole, of the liquid has distilled. (See first fractionation in the example, p. 7.)

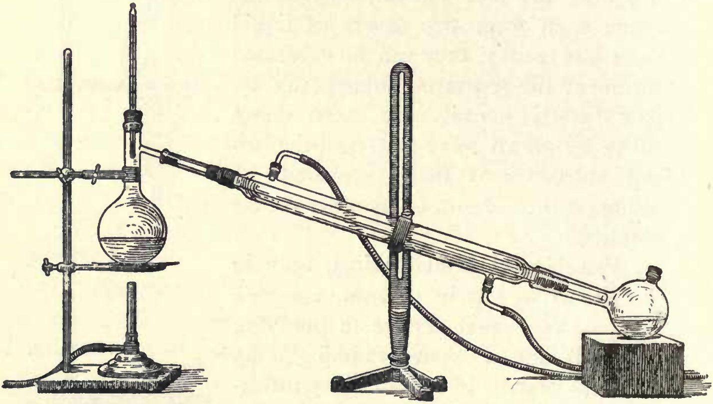

FIG. 2.

The distillation flask is then cleaned, and fraction No. 1 is returned to it and redistilled; that which comes over between the same intervals as before is collected in No. 1 receiver, and the distillation is stopped whilst No. 2 fraction is returned to

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[1] Reference may be made, if required, to "Distillation," vol. ii., Watts' "Dict.," new edit.; and also Thorpe's "Dict. App. Chem.," vol. i.

the flask, which is again heated, and all that which comes over between the same degrees as the last is added to No. 1 receiver. Then that which comes over during the second interval is collected in No. 2 receiver; when fraction 3 is added and a similar course pursued as with fraction 2, till the whole has been refractionated.

This system of redistillation is repeated as many times as is necessary, and it is usually found that the liquid tends to form large "fractions" at certain intervals of temperature (see the third to sixth fractionations in the example given). If these larger quantities are refractionated using smaller differences of temperature, eventually pure compounds may be obtained.

The following example, due to Kreis, will illustrate the method. The mixture used was composed of equal weights of benzene and toluene.

Temperature intervals.	Fraction.	Volume of distillate in c.c.					
		First fractionation.	Second fractionation.	Third fractionation.	Fourth fractionation.	Fifth fractionation.	Sixth fractionation.
81–84.......	1	1·0	9·0	17·0	19·5	21·5	22·0
84–87.......	2	10·0	9·5	7·0	5·5	4·5	3·5
87–90.......	3	14·5	8·5	4·5	4·0	3·0	2·0
90–93.......	4	8 0	5·0	3·5	2·5	1·5	1·5
93–96.......	5	6·0	3·5	3·0	2·0	2·0	1·0
96–99.......	6	5·5	3·5	2·0	2·5	1·5	1·0
99–102......	7	2·5	2·5	2·5	1·5	1·5	1·0
102–105. ..	8	3·5	4·0	2·5	2·0	1·5	1·0
105–108....	9	3·5	3·5	2·5	1·5	1·5	1·5
108–111....	10	3·5	7·5	10·5	13·0	4·5	16·0

Experiment 1.—Fractionally distil a mixture of 50 c.c. benzene, b.p. 80·5°, and 50 c.c. toluene, b.p. 110°, collect the fractions every five degrees, and note the large fractions near 81° and 110° respectively.

The separation into large fractions occurs more rapidly if a modified still head, such as suggested by Wurtz (Fig. 3), or if the dephlegmating apparatus of Linnemann (Fig. 4), Le Bel and Henniger (Fig. 5), or Glinsky (Fig. 6), is employed.

A simple column filled with glass beads (Hempel) will also answer the same purpose. All these pieces of apparatus hasten the separation of the constituents of a mixture because they effect a partial condensation of the vapours of the higher-boiling liquids, which thus flow back to the boiling flask and distil over at a higher temperature later.

In some cases it is necessary, so as to prevent the decomposition of the substance, to distil it under low pressure, in which case the receiver is fitted air-tight to the condenser and connected with some form of air-pump which will produce the necessary lowering of pressure, and consequent reduction of boiling point.

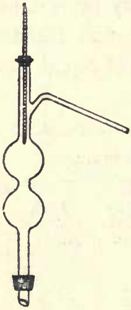
FIG. 3.

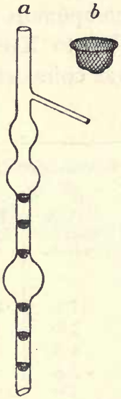

FIG. 4.

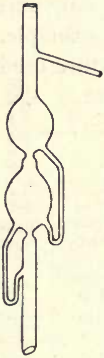
FIG. 5.

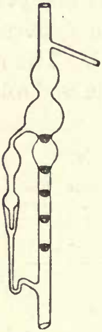
FIG. 6.

Distillation in a Current of Steam serves in some cases to separate a compound from impurities which are not volatile under the same conditions; and in other cases aids the distillation of compounds which would otherwise decompose at ordinary pressures. The apparatus for this purpose may be arranged as in Fig. 7, in which the first vessel is a tin can which serves as a boiler for providing the steam, which is blown in a rapid current through the liquid in the flask. The volatile substance is then found either dissolved in, or mixed with water, in the condenser, and is freed from water by extraction with ether, or by other suitable means.

Experiment 2.—Fit up the apparatus, Fig. 7, and distil some aniline and water in it, and notice that aniline is present in the distillate.

4. **Fractional Precipitation** frequently enables us to separate substances from each other. So, if a solution of magnesium acetate is added in small quantities at a time to an ammoniacal alcoholic solution of fatty acids, a series of precipitates is obtained of different compositions. The first fraction will contain principally the salt of the acid of *highest* molecular weight, and the last that of the *lowest*. By decomposing the fractions with HCl and refractionating them, a fairly complete separation of the mixture is eventually obtained.

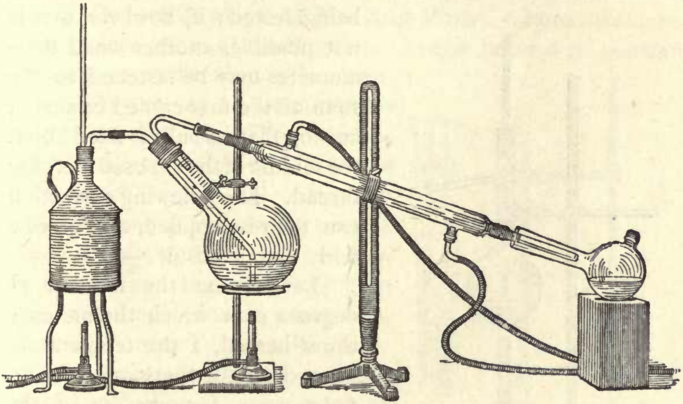

FIG. 7.

DETERMINATION OF THE PURITY OF COMPOUNDS.

If possible, the purity of an organic compound should always be checked before analysis, by a determination of either its *boiling* point or its *melting* point. Substances to which these tests cannot be applied, must be purified until they are shown by analysis to possess the theoretical percentage composition; or, if they are newly discovered bodies, until after repeated purification they are found to have an unvarying composition.

1. **Determination of Boiling Point.**—Every substance

capable of ebullition without decomposition possesses, *if pure*, a *constant* boiling point, and the determination of this "constant" is very important for confirming the purity of such a body.

The ordinary method of performing the operation is to place some of the compound in a tubulated distillation flask fitted with a thermometer as shown in Fig. 8. Heat is then applied, and as soon as the thermometer is constant the temperature is noted. If possible, the whole of the mercury thread should be exposed to the vapour of the substance being tested; if, however, that is not possible, another small thermometer may be fastened to the stem of the first-named in such a fashion that its bulb is fixed about the middle of the exposed mercury thread. The following correction can then be applied, and gives a fairly correct result:—

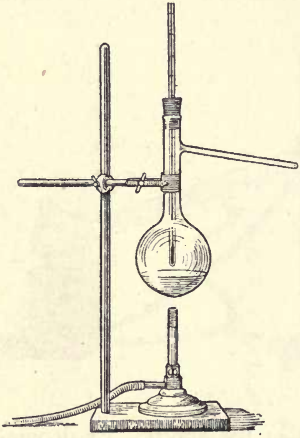

FIG. 8.

Let N be the number of degrees over which the mercury is *not* heated, T the temperature as read on the thermometer, and t the mean temperature of the mercury column not heated by the vapour (this is given by the small thermometer). The correction to be *added* to the observed temperature is $0{\cdot}000143(T - t)N$.

In accurate determinations, the barometric reading should be taken and corrected to 0°. The following corrections may be applied:—

(i.) For water or the lower alcohols, $\theta = (p - 760)\frac{273 + t}{10000}$; (ii.) for other liquids, $\theta = (p - 760)\frac{273 + t}{8200}$, where θ is the true boiling point, p the atmospheric pressure, and t the observed boiling point.

If the amount of substance to be tested is small, since the vapour will easily become superheated, too high a temperature may be registered. This may be prevented by wrapping round the bulb of the thermometer either a *little* cotton wool or, for high temperatures, a little asbestos, which keeps the bulb moist.

Experiment 3.—Determine the boiling points of absolute alcohol and of aniline by the method described, and in the latter case apply the correction for the mercury thread exposed to the air.

2. **Determination of Melting Point.**—Pure substances which fuse without undergoing change possess a constant melting point, which may be determined by the aid of the apparatus shown in Fig. 9. This consists of a small test-tube, or a piece of thin quill tubing, 4–5 mm. in diameter, which is drawn out into a capillary of about 1·5 mm. external diameter, and the fine end of the tube fused up. For the estimation, a small portion of the solid whose melting point is required is introduced into the tube at the top of the capillary portion. The tube is fastened by means of fine wire or a small indiarubber ring to the bulb of a delicate thermometer, as shown in the figure. The whole is next suspended in a beaker that contains a transparent liquid which boils at a higher temperature than that required to liquefy the solid. The liquid is then gently heated while being continuously stirred by the twisted glass rod. As soon as the substance melts, the temperature is noted. This experiment should be repeated two or three times, and the mean of the results taken as the correct melting point.

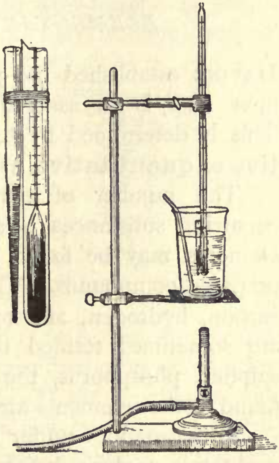

FIG. 9.

For certain substances, *e.g.* fats, it is advisable to leave the end of the tube *open*. Some of the compound is then melted and the fine end of the tube inserted in it. That which enters is allowed to solidify there, and the tube is attached to the thermometer and heated in the bath as before; but the temperature at which the liquid rises in the tube is taken as the melting point of the solid.[1]

Experiment 4.—Ascertain the melting points of chloral hydrate and of urea, after drying them between filter paper.

CHAPTER III.

ELEMENTARY ORGANIC ANALYSIS.

HAVING established the purity of an organic substance, the next step is to ascertain its **elementary composition.** This is determined by **ultimate analysis**, either **qualitative** or **quantitative**, as may be requisite.

The number of elements usually present in naturally occurring substances is small, although most of the known elements may be found in one or other of the artificially prepared compounds. The ordinarily occurring elements are carbon, hydrogen, and oxygen, more rarely nitrogen; these are sometimes termed the **organogens.** Less frequently sulphur, phosphorus, the halogens, arsenic, and silicon are found; other elements are rarely present.

All substances under investigation must be subjected to qualitative analysis before they are quantitatively examined, as their qualitative composition frequently determines the method to be employed for their quantitative analysis. In the following pages the qualitative tests for the elements immediately precede and are associated with the like quantitative ones.

Carbon and Hydrogen.—Carbon may frequently be detected by the blackening which occurs when the substance

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[1] When a solid has had to be melted for insertion in the tube, it is best to allow it to remain a day before taking the melting point; this precaution will obviate inaccurate results in those cases where an abnormal result is obtained after recent fusion.

is heated on platinum foil or in a test-tube. If the discoloration is due to separated carbon, this will disappear wholly or in part on continued ignition, and only leave as ash any metallic residue. Blackening due to the separation of carbonaceous matter also often happens when a compound is heated with concentrated sulphuric acid.

Many compounds, however, do not give these results, in which case the carbon may be detected either by burning them in a current of oxygen, or by mixing them with cupric oxide in a tube, and heating the mixture to redness. By these means the carbon is oxidised to CO_2, which is detected by passing the evolved gases through lime-water. A simple apparatus, such as shown in Fig. 10, may be employed for performing this test, and will at the same time demonstrate the presence of hydrogen by the condensation of moisture which will occur in the bulb-tube. If the amount of substance tested is small, the hydrogen can be detected best by passing the gases over dry P_2O_5, which readily deliquesces in the presence of moisture. Of course, for these tests the substance itself must be perfectly dry.

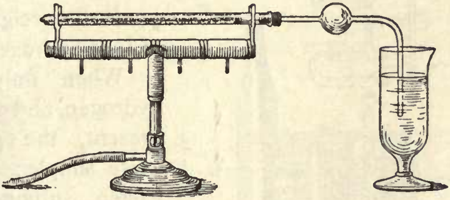

FIG. 10.

Experiment 5.—Prove the presence of carbon and hydrogen in sugar, starch, or gelatine by either of the above methods.

For the **Quantitative Estimation** of **Carbon** and **Hydrogen**, the method employed to-day is essentially that devised by Lavoisier, which was carried to a high state of perfection by Liebig. It depends upon the reaction just illustrated in describing the qualitative detection of these elements, *i.e.* oxidising them to carbon dioxide and water either by means of oxygen or air, or of some oxidising substance such as CuO or $PbCrO_4$. The weights of the carbon dioxide and water produced from a given weight of material are ascertained, and from them the corresponding amounts of carbon and hydrogen are easily calculated, because $\frac{3}{11}$ of the weight of the CO_2 is carbon, and $\frac{1}{9}$ of the weight of the H_2O is hydrogen.

When only carbon, hydrogen, and oxygen are present, the process is quite simple; but if nitrogen, sulphur, or the halogens occur, it requires suitable modification.

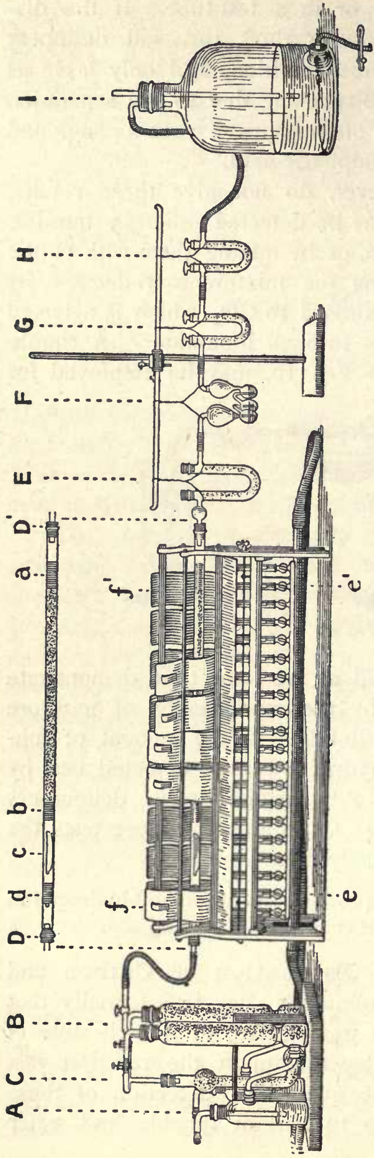

Fig. 11.

Open-Tube Method.—The method which is now usually employed may be called the open-tube method, to distinguish it from the earlier or closed-tube process, in which one end of the combustion tube is closed by fusion.

The combustion is performed in a current of air or of oxygen, and aided by copper oxide, and the products are absorbed by calcium chloride or concentrated sulphuric acid, and caustic potash or soda-lime respectively.

The process is carried out as follows, in the apparatus shown in Fig. 11. A tube, DD′, about 85 cm. in length, 14–16 mm. in diameter, and made of hard Bohemian glass 1·5–2 mm. thick, is thoroughly cleaned and dried. A strip of copper gauze *a*, 25–30 mm. wide, is made into a roll which fits the tube tightly, and pushed into it to about 3 cm. from one end. The tube is next filled to within 25–30 cm. of the other end with copper oxide, preferably made from wire, which is kept in position by another roll of gauze *b*. A space is then left for the introduction of the platinum or porcelain boat *c*, and another plug of wire gauze arranged to be easily removable is put in at *d*.

The tube so prepared is placed in a combustion furnace, which in the illustration is Erlenmeyer's furnace, and consists essentially of a number of Bunsen burners, *e*, *e′*, the flame of which plays directly upon the trough that supports the tube, is there deflected, and then thrown down again upon the combustion tube by the movable tiles, *f f′*.

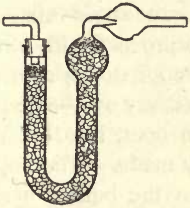

FIG. 12.

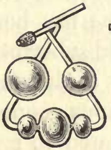

FIG. 13.

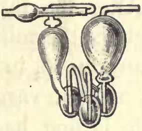

FIG. 14.

At the end of the tube farthest from the boat there are attached to it, in order, the U-tube E, filled with granulated calcium chloride or with broken pumice or glass beads moistened with strong sulphuric acid, for the absorption of the water; Geissler's bulbs F, filled with strong potash, and the U-tube G, with soda-lime, in which the carbon dioxide is absorbed. The U-tube H is filled with calcium chloride, and serves to prevent any moisture passing back from the aspirator I. A useful $CaCl_2$ tube is shown in Fig. 12, and the potash bulbs, which may be either Liebig's or Geissler's, are shown in detail in Figs. 13 and 14.

The air or oxygen which is used during the operation is stored in a suitable gas-holder, and is dried and freed from carbon dioxide by bubbling it through strong sulphuric acid in the vessel A, then passing it through the eprouvette B, which is packed at the bottom with soda-lime and at the top with calcium chloride, and finally through the U-tube C, which also contains calcium chloride. The aspirator I may be employed either to keep a slightly diminished pressure in the tube during the operation, or for drawing air through the apparatus instead of forcing it through from a gas-holder.

It is necessary, before making a combustion, to thoroughly dry the copper oxide, and also to free it from all traces of organic matter. This is done by heating the tube and its contents to redness for some time while passing through it a current of dry air. Since, too, the first analysis which is made with the apparatus is almost invariably incorrect, it is customary to make one or more combustions of cane-sugar first, and when a correct result is obtained, then to proceed with others.

After the tube has been allowed to cool down, a known weight of the solid substance to be analysed, say 0·25–0·30 gm., is introduced, in a platinum or porcelain boat, into the tube at *c*, and the various connections carefully made. The copper oxide is first heated to redness, and then the burner nearest to the boat is lighted, and the substance gradually heated while a slow current of oxygen is sent through the apparatus. The heat is increased gradually, and the passage of oxygen continued until the gas passes unabsorbed through the potash bulbs, when it is discontinued, and air is passed through to displace it in those tubes which have to be weighed. These are then disconnected, wiped clean, and weighed, after cooling for about half an hour.

In the presence of nitrogen, the halogens, or sulphur, certain modifications are necessary.

When **nitrogen** is present, a roll of bright copper gauze, about 10–12 cm. in length, or a layer of reduced copper oxide, must be placed at the end of the tube nearest the potash bulbs. If this is kept at a bright red heat, it decomposes the oxides of nitrogen, which are formed during the combustion, and would otherwise be absorbed by the potash. The copper may be replaced by a layer of precipitated manganic hydrate, which has been made into a paste with a saturated solution of K_2CrO_4 containing 10 per cent. of $K_2Cr_2O_7$, dried and granulated. This is heated to a black heat (about 200°) during the combustion, and absorbs the nitrogen oxides.

When **halogens** are present the copper must either be replaced by silver foil, or the whole or part of the CuO replaced by lead chromate. The latter compound should also be used in the presence of **sulphur** or **phosphorus.** The lead retains the halogens, sulphur, etc., as lead salts, etc., otherwise the halogens, sulphur dioxide, etc., would pass into the potash bulbs and be absorbed and weighed there.

The directions just given apply when the substance is solid; if liquid and non-volatile, it may be treated in the same way. If, however, the liquid is volatile, the process must be modified according as it is difficultly or easily vaporised. In the former case, it is weighed in a quill tube sealed at one end, and having the other drawn into a capillary, and which is subsequently introduced into the boat. In the latter case, special arrangements have to be made for vaporising it at a slow rate *outside* the combustion tube.

Closed-Tube Method.—In the older or closed-tube method, a tube of hard glass about 45 cm. in length and 1·2–1·5 cm. in diameter is drawn out as shown in Fig. 15, and, after being thoroughly cleaned and dried, is filled as far as *a* with granulated and ignited copper oxide. About 0·5 gram of the substance to be analysed is then introduced in intimate mixture with powdered copper oxide, and fills up the distance *a* to *b*; the mortar or other vessel used for mixing is rinsed out with more powdered copper oxide, filling the tube to *c*, and from *c* to *d* is filled with the granulated oxide, which is kept in position by a plug of copper gauze or asbestos. The tube is tapped gently so as to cause a

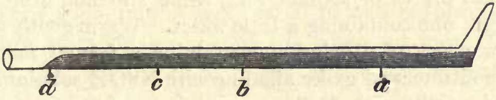

Fig. 15.

passage for the gas all along the tube, and is then fitted with absorption tubes as described above. During the combustion the granular oxide is first heated to redness, and then the oxide mixed with the compound to be analysed is heated little by little. Finally, when no more gas passes into the absorption bulbs, the end of the tube is broken off, and a current of air freed from carbon dioxide and water is aspirated through the apparatus.

Nitrogen.—1. If the substance tested is not a compound which contains a nitro (NO_2), nitroso (NO), azo, or diazo (—N=N—) group, the nitrogen may be readily detected by heating it with *recently ignited* soda-lime,[1] when ammoniacal vapours will be evolved, recognisable by their smell and their action on turmeric paper.

Experiment 6.—Show the presence of nitrogen in hair, albumen, or cheese by igniting with soda-lime, and testing for ammonia in the evolved gases.

2. A more delicate test for nitrogen, applicable to *all but diazo-compounds*, depends upon the formation of a cyanide when the compound is strongly heated with potassium or sodium; if the substance is explosive, dry sodium carbonate must be also mixed with it; and if sulphur is present, fine iron filings or reduced iron must be added, to prevent the formation of thio-cyanate. The cyanide can then be detected by the formation of Prussian blue, as described in Experiment 7.

Experiment 7.—Ignite a little dry urea, in a test-tube, with one or two *small* pieces of sodium, and, while still hot, drop the tube into a larger one containing a little water. Warm gently and filter. Add a few drops of a solution containing a ferrous and a ferric salt to the filtrate, and make alkaline with NaOH solution. Warm gently and acidify with HCl; a precipitate of Prussian blue will show the presence of nitrogen.

Quantitative Estimation.—Nitrogen may be estimated by converting it into ammonia and determining it as such (Will and Varrentrap, Kjeldahl), or else it may be measured as nitrogen (Dumas).

Will and Varrentrap's method is not available for nitro,

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[1] Prepared by slaking two parts good CaO in a solution of one part NaOH free from nitrates, drying, and then igniting the mixture.

nitroso, azo, or diazo bodies, and occasionally the nitrogen cannot be determined in other substances by its means. It depends upon the fact that many compounds, when heated with NaOH or KOH, yield their nitrogen as ammonia, while the carbon is oxidised to CO_2.

For carrying out the determination, a piece of combustion tubing about 40 cm. long is fused up at one end, as shown in Fig. 16.

About 5 cm. of dry oxalic acid or powdered magnesite is put into the tube, and then a little soda-lime. About 0·3 gram of the substance for analysis is intimately mixed in a mortar with sufficient powdered soda-lime to form a layer 12–15 cm. long; this is poured into the tube, the mortar rinsed out with a little more of the powder, and finally the tube is filled to within 4 cm. of the mouth with the granular soda-lime. A plug of asbestos is introduced, and the tube can then be attached by means of a cork to the absorption bulbs, which contain a solution of sulphuric or hydrochloric acid.

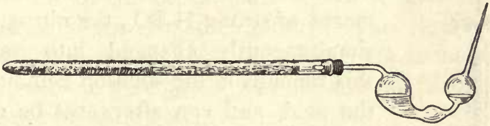

FIG. 16.

The tube is then heated in a furnace. Beginning at the open end the soda-lime is first heated to dull redness, and then the mixture is gradually ignited till, when no more ammonia is evolved, the last traces of it are swept out by heating the oxalic acid.

Two courses are now open to the operator. If the acid employed is hydrochloric acid, platinum chloride can be added, and the platino-ammonio-chloride collected, dried, ignited, and the resulting platinum weighed. Now, since by the formula $(NH_4)_2PtCl_6$, 195 of Pt are equal to 28 of nitrogen, the percentage of the nitrogen present is readily calculated.

It may be more convenient, however, to employ a solution of acid of known strength. The amount of acid neutralised during the combustion is then a measure of the nitrogen evolved as ammonia (see Example, p. 24).

If the substance analysed contains a large percentage of nitrogen, it should be mixed with some sugar, so as to dilute the ammonia and cause more regular absorption.

If the compound is liquid, it may be mixed with the soda-lime in the manner described under the estimation of carbon and hydrogen. If reducing substances are added to the soda-lime, the method described is much more widely applicable.

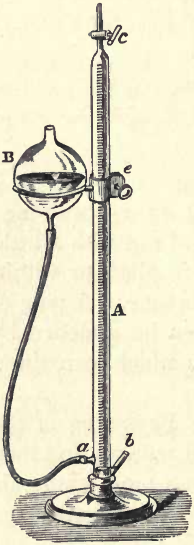

Fig. 17.

The nitrogen in a large nmmber of compounds can be determined by **Kjeldahl's method,** which essentially consists in oxidising the carbonaceous matter by means of strong H_2SO_4, the nitrogen being simultaneously changed into ammonia; this remains in the solution combined with the acid, and can afterwards be obtained from it by decomposing the salt with excess of alkali, and estimating the evolved ammonia in the ordinary manner.

In **Dumas' process** or its modifications, the compound is burnt with copper oxide, and the nitrogen collected as such.

A piece of combustion tubing about 80 cm. long is closed at one end by fusion and filled with the following substances, in order: sodium bicarbonate for about 15 cm., then a little copper oxide, next a mixture of 0·3–0·6 cm. of the substance to be analysed with powdered cupric oxide, followed by the rinsings, and finally granular oxide up to within 16–18 cm. of the open end. A roll of copper gauze 10–15 cm. long is then introduced, and the tube fitted with a cork and tube for connection with the vessel employed for collecting the gas.

For this purpose Schiff's burette, shown in Fig. 17, is very useful, and consists of a burette graduated from the top and fixed into a heavy foot. A movable reservoir, B, is connected by indiarubber tubing to a tubulus at *a*. Mercury is then poured in through the tubulus *b*, which is at an angle of 45°, till it is 2–3 mm. above the lower opening. A strong solution of caustic potash is then put in the reservoir, and the burette filled with that, while the tubulus *b* is closed with a cork, and the reservoir then lowered.

The combustion tube is now placed in the furnace, and the air entirely driven out by heating part of the sodium bicarbonate. When this has taken place (which is ascertained by inserting the exit tube into the tubulus *b*, and watching whether the gas is *almost* totally absorbed by the potash), the combustion is performed in the ordinary manner, till at its close the rest of the bicarbonate is heated and all traces of nitrogen are swept into the burette. The reservoir is now raised till the liquid in it and the burette are at the same level, when the volume V of gas is read off, and the temperature and atmospheric pressure noted.

The weight W of nitrogen can be found from the formula—

$$W = V \times 0{\cdot}001256 \times \frac{P - T}{760} \times \frac{273}{273 + t}$$

$$\text{or } W = \frac{V(P - T)0{\cdot}001256}{(1 \times 0{\cdot}00366t)760}$$

where P is the barometric pressure, t the temperature at time of measurement, T the pressure of aqueous vapour, and 1 c.c. of nitrogen at N.T.P weighs 0·001256 gram.

The calculation may be much facilitated by tables, which give the weight of 1 c.c. of nitrogen at any temperature and pressure within ordinary limits.

Halogens.—The presence of these elements may be shown by fixing a lump of copper oxide in a platinum wire, strongly igniting it, then dipping it in the haloid substance, and again igniting it, first in the inner, and finally in the outer flame: a green flame indicates a halogen compound. They may also be detected by suitable modifications of the two following methods, which are employed for their estimation.

1. **Ignition with Lime.**—The haloid compound is mixed with pure lime, or, better, with soda-lime, and ignited in a combustion tube closed at one end; the contents are

then dissolved in nitric acid, and the halogen estimated as the silver salt by precipitation with silver nitrate.

2. **Carius' Method.**—In this process the organic substance is oxidised by heating to a high temperature with strong nitric acid. A piece of strong glass tubing is well fused up at one end. About 4 c.c. of strong nitric acid and 1 gram of silver nitrate are placed in it, and a thin *weighed* and closed tube containing about 0·5 gram of the substance is then introduced. The tube is now drawn out to a thick point, and the end carefully fused up, as in Fig. 18, is shaken so as to fracture the small bulb, and is then introduced into an air-bath, such as shown in Fig. 19.

Fig. 18.

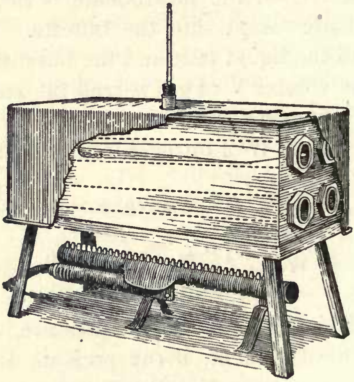

Fig. 19.

This contains four stout iron tubes, which can be covered over by a loose case. In this air-bath the tube is heated for two hours to a temperature which varies from 160° to 250°, according to the substance analysed (frequently the tubes burst, but damage is prevented by the cover). The tube is then allowed to become perfectly cold, is wrapped round with a cloth, and the extreme point softened in a Bunsen flame. The gas inside, being under pressure, forces its way through the softened part, and when it has escaped, the end of the tube is cut off, and the silver salt and fragments of glass bulb are collected and weighed, and from the weight of the silver haloid the percentage of halogen can be calculated.

Experiment 8.—Test for the presence of halogens, by means of copper oxide as above, in chloroform, ethyl or methyl bromide, and iodoform.

Sulphur may be detected (1) by igniting the suspected substance with sodium, and adding sodium nitro-prusside to an aqueous solution of the residue, when a violet coloration indicates the presence of that element. (2) It may also be detected or estimated by fusion with a mixture of four parts *pure* dry sodium carbonate and one part potassium nitrate. The resultant product is then dissolved in hydrochloric acid, and the sulphate precipitated as barium sulphate; or (3) volatile substances may be heated with nitric acid, as in Carius' halogen method, and the sulphate precipitated in the ordinary way.

Experiment 9.—Test for sulphur in egg albumen by the first method.

Phosphorus.—This element can be detected and estimated by either method 2 or method 3 given for sulphur, the phosphorus being detected by solution of ammonium molybdate, and estimated by precipitation as magnesium ammonium phosphate. It may also be detected by carbonising the substance, and then igniting it with magnesium powder. The product, which contains magnesium phosphide, glows in the dark, and gives off PH_3 when moistened with water.

Experiment 10.—Try the last test for phosphorus, employing yolk of egg for the purpose.

Oxygen is usually estimated by difference. The direct methods proposed are not satisfactory.

CHAPTER IV.

PERCENTAGE COMPOSITION—EMPIRICAL FORMULÆ.

Percentage Composition.—From analytical results obtained by the methods described, it is easy to calculate the percentage composition of a given substance, and from that to ascertain the **ratio** of the number of atoms in the molecule to each other.

The following results actually obtained in the analysis of **urea** will illustrate the method employed.

0·481 gram of urea was burnt in a current of oxygen, and yielded 0·2918 gram of water and 0·363 gram of carbon dioxide.

The percentage amount of hydrogen present in the urea is 6·76—

$$\text{for } 0{\cdot}2918 \times \frac{1}{9} = 0{\cdot}0324 \text{ H, and } 0{\cdot}0324 \times \frac{100}{0{\cdot}481} = 6{\cdot}76$$

The percentage amount of carbon is 20·11—

$$\text{for } 0{\cdot}363 \times \frac{3}{11} = 0{\cdot}099 \text{ C, and } 0{\cdot}099 \times \frac{100}{0{\cdot}481} = 20{\cdot}11$$

0·300 gram of the urea was ignited with soda-lime, and 10 c.c. of normal (**N**) sulphuric acid was neutralised by the ammonia evolved.[1] Now, 1 c.c. of (**N**) H_2SO_4 = 0·049 gram H_2SO_4, and is equivalent to 0·017 gram NH_3, or 0·014 gram N.

Therefore the percentage amount of nitrogen present is

$$10 \times 0{\cdot}014 \times \frac{100}{0{\cdot}3} = 46{\cdot}66$$

The percentage composition, then, of urea is C, 20·11; H, 6·76; N, 46·66; and O (by difference), 26·47 per cent.

Empirical Formula.—From the percentage numbers the empirical formula of urea can be readily calculated in the usual manner by dividing those numbers by the atomic weights of the respective elements, and calculating the ratios of the nnmber of atoms to each other. Thus—

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[1] For an example in which the NH_3 is precipitated as $(NH_4)_2PtCl_6$, see Appendix, p. 281.

Percentage composition. Ratio.

$C = 20{\cdot}11 \div 12 = 1{\cdot}67 = 1$

$H = 6{\cdot}76 \div 1 = 6{\cdot}76 = 4$

$N = 46{\cdot}66 \div 14 = 3{\cdot}33 = 2$

$O = 26{\cdot}47 \div 16 = 1{\cdot}65 = 1$

or the simplest formula for urea is CH_4N_2O.

This process of analysis and calculation serves one of two ends: (1) either to assist us in the identification of a known body; or (2) it is the first step in fixing the formula of a substance hitherto unknown. Whether the empirical is also the molecular formula depends upon other facts, which will be considered in the next chapter.

CHAPTER V.

DETERMINATION OF MOLECULAR FORMULÆ.

In order to establish the molecular formula of a substance, it is necessary to determine its molecular weight. The methods applicable to such an end differ with the nature of the compound under consideration.

1. If the substance is volatile, it is sufficient to determine either the vapour density, or specific gravity of its vapour.

2. If it is not volatile, nothing could be done till recently except to study its chemical properties, and from its different combinations and decompositions draw conclusions as to its molecular weight. Latterly, however, several methods have been devised which can be employed, provided only that the body is capable of solution in some suitable medium. The principal of these are (i.) Raoult's method of determining the molecular reduction of freezing point, and (ii.) Beckmann's and Wiley's process of finding the molecular increase of boiling point. The first only will be described.

3. When physical methods such as the preceding are not available, chemical methods are resorted to; thus if the substance is non-volatile, and either acid or basic, its basicity or acidity is determined, and its molecular weight ascertained

from the analysis of it and its salts. If it is a neutral substance, then its substitution derivatives, and its oxidation and other products are examined, and from the results, it is frequently possible to form just conclusions as to the molecular formula of the substance. These methods are not, however, so satisfactory as the preceding ones.

1. DETERMINATION OF VAPOUR DENSITY.

Three methods can be employed for this purpose; namely, those due respectively to Hofmann, Dumas, and V. and C. Meyer. The difference in principle between these processes should be carefully noted: thus, in Hofmann's method the volume of vapour produced by a known weight of material is found; Dumas finds the weight of material *after* vaporising it, and then determines its volume; while, finally, the Meyers measure the volume of *air* displaced by a given weight of material when in a state of vapour. Of course, in all these methods the temperature of measurement and the barometric pressure are duly recorded.

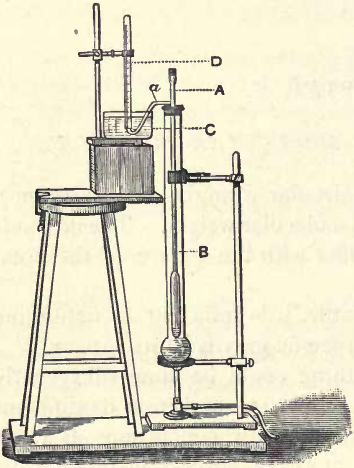

FIG. 20.

Of these three processes, that due to the Meyers finds most frequent use in organic investigations on account of its simplicity, and will therefore be described more fully than the other two.

Meyers' Method.—The essential apparatus in this process is the vapour-tube A (Fig. 20), which consists of a tube about 50 cm. long, on the lower end of which is blown an elongated bulb of about 150 c.c. capacity. The upper end of the tube is slightly enlarged so as to receive a cork, and about 10 cm. from the top the bent capillary tube *a* is fused into it. The whole is fitted by means of a cork into the wide glass vessel B, which serves as boiler and vapour jacket. Besides this, a glass dish C, a graduated measuring-tube D, and a stoppered tube sufficiently small to drop down the tube A, are required. The entire apparatus may be fitted together in some such manner as indicated.

The following is the method of use :—

Water or other liquid of known and *constant* boiling point is placed in B and heated to free ebullition, and the carefully dried and stoppered tube A thus heated until no further expulsion of air occurs. The measuring tube filled with water is next brought over the mouth of the capillary tube *a*, and, lastly, the little weighing bottle *full* of a weighed portion (0·05–0·2 gram) of the substance is dropped into A, the cork being rapidly withdrawn and replaced for that purpose.[1] The heat of the apparatus causes the substance in the weighing bottle to volatilise, and it loosens the stopper and drives a quantity of air over from A into D.

When no further expulsion of air occurs, the tube D is removed and immersed in a deep vessel of water so as to bring it all to one temperature, and the volume of air collected is read off when the level of the water inside the tube is coincident with that of the water outside it. The data required for the calculation of the vapour density are (i.) The volume V of air expelled ; (ii.) the temperature t of the air at the time of measurement ; (iii.) the barometric pressure P in mm. ; (iv.) the pressure T of aqueous vapour in mm. ; (v.) the weight W_1 of substance taken ; and (vi.) the weight W of a volume of hydrogen equivalent to the volume of the expelled air, and therefore equivalent to the volume of the substance vaporised.

Then $\text{V.D.} = \frac{W_1}{W}$, and W can be found from the expression—

$$V \times 0{\cdot}0000896 \times \frac{P - T}{760} \times \frac{273}{273 + t}$$

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[1] A layer of asbestos is usually placed at the bottom of A, to prevent its fracture.

where 0·0000896 is the weight in grams of 1 c.c. of hydrogen at 0° C. and 760 mm.

Example.—0·2162 gram of chloroform expelled 43·7 c.c. of air when vaporised in Meyers' apparatus. The temperature of the air was 18° C.; the barometric pressure was 760·5 mm.; and the pressure of aqueous vapour at 18° C. is 15·4 mm.

By the formula above—

$$\frac{W_1}{W} = \frac{0·2162}{43·7 \times 0·0000896 \times \frac{760·5 - 15·4}{760} \times \frac{273}{273 + 18}} = 60·03$$

Dumas' Method.—The apparatus for this process is illustrated in Fig. 21, the essential part being the glass bulb A, of about 250 c.c. capacity, which is weighed dry and empty. An unknown weight, say 5–10 grams of substance, is then placed in it and volatilised by heating in the bath. When the excess of the substance is driven out and the bulb is full of vapour, it is sealed at the neck by means of a blowpipe flame. The bulb is then wiped, cooled, and weighed.

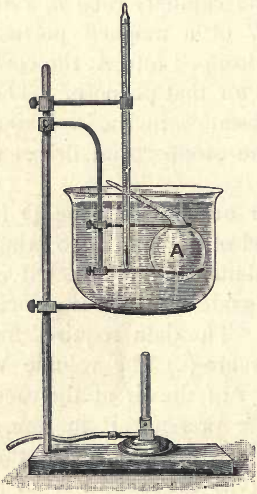


FIG. 21.

The temperature T of the bath at the time of sealing, the barometric pressure P at the same time, and the temperature t and barometric pressure p at the second weighing, are noted. Besides these data, the weight w_1 of the empty bulb, the apparent weight w_2 of the bulb and vapour, and the capacity C are required;

Then, as before, $\text{V.D.} = \frac{W_1}{W}$

Now, since the true weight of the vapour is equal to the apparent weight $(w_2 - w_1)$ plus the weight of the volume of air displaced by the bulb during weighing—

$$\therefore \text{V.D.} = \frac{W_1}{W} = \frac{w_2 - w_1 + \left(C \times 0·001293 \times \frac{p}{760} \times \frac{273}{273 + t}\right)}{C \times 0·0000896 \times \frac{P}{760} \times \frac{273}{273 + T}}$$

where 0·001293 is the weight in grams of 1 c.c. air at 0° C. and 760 mm.

Hofmann's Method.—The apparatus for this is shown in Fig. 22, and consists essentially of the long graduated vapour tube A, which is surrounded by the vapour jacket B. At the commencement of the operation A is filled with mercury, so that when a weighed portion of the substance is introduced in a tiny bottle at the bottom of the tube, it rises at once to the top of the mercury, and is vaporised under considerably reduced pressure by the heat obtained by blowing steam or other vapour into the jacket from the boiler C.

Then, as before, $\frac{W_1}{W}$ gives the vapour density, W_1 being known, and W can be calculated by the aid of the following data: (i.) the volume V of the vapour, (ii.) the temperature t of the vapour, (iii.) the height p of the mercury column in A, and (iv.) the barometric pressure P, and the full expression is—

$$\text{V.D.} = \frac{W_1}{W} = \frac{W_1}{V \times 0{\cdot}0000896 \times \frac{P - p}{760} \times \frac{273}{273 + t}}$$

Now, since the number representing the vapour density (specific gravity H = 1) of a compound is half that which represents its molecular weight, that number only requires doubling in order to fix the weight of the molecule. If, however, the specific gravity is calculated against air = 1, the relation is expressed by the formula: mol. wt. = sp. gr. $\times\ 14{\cdot}44 \times 2 \left(\frac{\text{sp. gr. air}}{\text{sp. gr. H}} = \frac{14{\cdot}44}{1}\right)$

By this means the results obtained from the analysis of a compound and the deduction of its empirical formula, can be confirmed or extended. Thus the empirical formula for chloroform, $CHCl_3$, represents a molecular weight of 119·5, and as an actual determination of its vapour density gave the number 59·38, which doubled becomes 119·76, it is evident that the empirical formula is in this case identical with the molecular formula. On the other hand, the empirical formula of hexane is C_3H_7, which equals 43; its vapour density experimentally determined

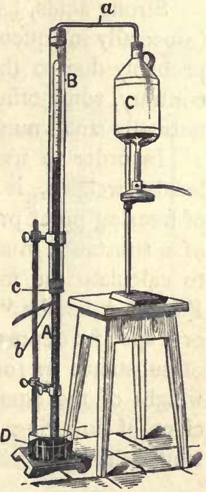


FIG. 22.

is 42·99, which doubled gives 85·98 as its molecular weight; consequently its empirical formula must also be doubled to bring the molecular formula into accordance with that result.

2. RAOULT'S CRYOSCOPIC METHOD.

When a substance is disolved in a solvent, the freezing point of which is known, and the liquid is frozen after the addition of such substance, it is found that the freezing point of the solvent is lower than before; and Raoult has proved by numerous researches that the amount of the depression is dependent both upon the substance dissolved and the solvent itself.

It has been further shown that molecularly equivalent weights of chemically similar bodies produce approximately the same depression in the same weight of a given solvent, provided that the solutions are *sufficiently dilute.*

Strong acids, bases, and salts (*i.e.* electrolytes) usually give (especially in aqueous solutions) an abnormally large depression, probably due to their dissociation when in solution. On the contrary, some other substances yield in certain solvents abnormally small numbers.

In order to use these facts for the determination of molecular weights, it is only necessary to observe the lowering of freezing point produced by the solution of a known weight of a substance in a given weight of solvent. It is then easy to calculate the molecular weight of the body in question. For let A be the "coefficient of lowering of freezing point" or "specific depression," produced by the solution of 1 gram of substance in 100 grams of solvent; if M is the molecular weight of the compound, then MA is the "molecular coefficient of lowering of freezing point" or "molecular depression = T.

$$\text{Consequently, if } MA = T \quad \therefore M = \frac{T}{A}$$

The general value of T for any solvent is ascertained by careful experiment with several different substances of known molecular weight. Approximate values for T are: water = 19, acetic acid = 39, benzene = 50, and nitro-benzene = 70.

The determination may be carried out in Beckmann's apparatus (Fig. 23), which consists essentially of a tube A, which contains the solvent; this is surrounded by the tube B, which serves as an air-bath, and which is in its turn immersed in C, which contains the freezing mixture. A delicate thermometer D graduated in $\frac{1}{100}$ of a degree is inserted into A, and both A and C have stirrers to keep their contents well mixed. The experiment is made as follows: C is filled with water or a freezing mixture 2°–5° below the freezing point of the solvent. A suitable weight, G, of the solvent, is introduced into A and stirred thoroughly; the temperature will sink below its freezing point, and, when a solid separates, will rise and become stationary. This is taken as the freezing point of the solvent. A weighed quantity, *g*, of the substance under examination is then introduced by the side-tube into A, and the freezing point again noted. From the difference of the readings the observed depression of freezing point, Δ, due to the dissolved substance, is found.

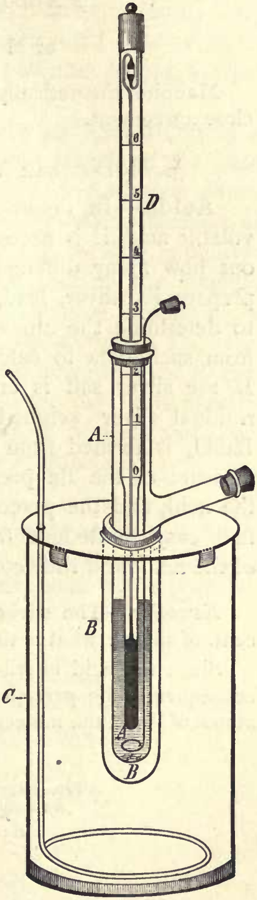


FIG. 23.

The specific depression A is then calculated by the proportion—

$$\left.\begin{matrix} g : 1 \\ 100 : G \end{matrix}\right\} :: \Delta : A, \text{ or } A = \Delta \frac{G}{g \times 100}$$

Example.—7·5382 grams of mannitol were dissolved in 95·09 grams of water, and the observed depression of freezing point was 0·835°. T = 19. By the formula given—

$$A = \Delta \frac{G}{g \times 100} = 0{\cdot}835 \times \frac{95{\cdot}09}{100 \times 7{\cdot}5382} = 0{\cdot}1052$$

$$\text{or } M = \frac{T}{A} = \frac{19}{0{\cdot}1052} = 180{\cdot}3$$

Mannitol theoretically is $C_6H_{14}O_6$ = 182, which is in sufficiently close agreement.

3. Molecular Weights of Acids and Bases.

Acids.—In determining the molecular weight of a non-volatile acid, it is necessary to ascertain its basicity by finding out how many different kinds of salts it can yield; next, to prepare its silver, lead, or barium salts in a pure state, and to determine the amount of the metal present in them, and from such data to calculate the molecular weight of the salt. If the silver salt is employed, it is dried, ignited, and the residual silver weighed; while if the barium salt is used, $BaSO_4$ is formed from it, and that is weighed and gives a measure of the Ba present. Then, knowing the basicity of the acid, and the percentage of silver or barium in the salt, it is easy to deduce from those data the molecular weight of the acid, and thus control its formula.

Example.—The silver salt of a tribasic acid contains 63·1 per cent. of silver: what is the molecular weight of the acid?

Since the acid is tribasic, its salt may be written $Ag_3\overline{Ac}$, and consequently the percentage of silver found is proportionate to 3 atoms of Ag in the molecule.

$$\therefore \begin{matrix}\text{Percentage of}\\ \text{Ag found}\end{matrix} : 3Ag :: 100 : \overset{\begin{matrix}\text{Mol. wt. of}\\ \text{silver salt.}\end{matrix}}{Ag_3\overline{Ac}}$$

$$63{\cdot}1 : 324 :: 100 : Ag_3\overline{Ac}$$

$$\therefore Ag_3\overline{Ac} = \frac{32400}{63{\cdot}1} = 513$$

And 513 − 324 of silver + 3 of hydrogen = 192, which is the molecular weight of the acid in question.

Of course, if the empirical formula yields a different number, it must be brought into accordance with this result.

Bases.—The molecular weights of basic nitrogenous substances can be found in a very similar fashion to that just described for acids. Just as two molecules of ammonium chloride combine with platinum tetra-chloride to form a well-defined double salt, so many hydrochloric acid salts of nitrogenous bases also combine with the platinum haloid to form definite compounds.

If, then, we can ascertain how many nitrogen atoms in a given compound possess basic properties, transform the base into the platinum compound, finally ignite it, and thus determine the amount of that metal present, we have a measure of the molecular weight of the base; since 1 atom of Pt is equivalent to 2 atoms of nitrogen, as will be seen by the formula $2R'HCl.PtCl_4$, where R' is a nitrogenous base containing 1 atom of basic nitrogen. But if Pt is equivalent to 2N, it is therefore equivalent to $2R'$, so that the magnitude of R' can be calculated if the percentage amount of the Pt is known. Of course, if the compound in question is di-acid, and contains two atoms of basic nitrogen, then Pt equals R''.

Example.—A substance containing carbon, hydrogen, and nitrogen was combined with hydrochloric acid and converted into a platinum salt. The platinum salt weighed 0·7516 gram, and yielded 0·2192 gram of metallic platinum: what is the probable molecular weight of the original substance?

In the compound—

$$\begin{array}{cccc} \text{Pt found.} & \text{At. wt. Pt.} & \text{Salt taken.} & \text{Mol. wt. of salt.} \\ 0{\cdot}2192 : & 195 :: & 0{\cdot}7516 : & 2R'HCl.PtCl_4 \end{array}$$

$$\therefore 2R'HCl.PtCl_4 = \frac{195 \times 0{\cdot}7516}{0{\cdot}2192} = 668{\cdot}6$$

$$\begin{aligned} \therefore 2R' &= 668{\cdot}6 - 2HCl.PtCl_4 \\ &= 668{\cdot}6 - 410 \\ &= 258{\cdot}6 \\ \therefore R' &= 129{\cdot}3 \end{aligned}$$

For further examples of the preceding calculations, see the author's "Chemical Calculations" (Longmans & Co.).

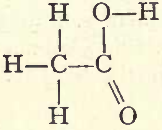
CHAPTER VI.

CONSTITUTION OF CARBON COMPOUNDS.

When the chemist has succeeded, by any of the methods described, in fixing the molecular formula of an organic substance, he has really only just commenced his study of it. He knows, it is true, the correct ratio of the number of atoms to each other, and also the total number of atoms in the molecule; but besides that, he desires to ascertain how these atoms are grouped together, and much further research is required in order to explain the structure of the molecule.

When this has been done, he is in a position to write the formula given to a substance in an extended fashion as a **Rational** or **Constitutional Formula.** For example, by a series of experiments it can be shown, *assuming carbon to be tetravalent*, that the formula of acetic acid, $C_2H_4O_2$, may be more fully expressed by the **constitutional formula** $CH_3.CO.OH$, which may be still further extended into the

Graphic Formula



Already, in writing the above formula, certain assumptions have been made; and in considering the constitution of organic bodies we have to be guided materially by the following considerations:—

1. The carbon atom appears to be constantly tetravalent, carbon monoxide is apparently an exception.

2. Carbon is remarkable for the facility with which it forms compounds with elements very diverse in their properties, and its affinity for hydrogen is especially noticeable.

3. Carbon atoms possess in a very special degree the power of linking with each other, and this linkage is remarkably stable.

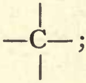
4. So far as can be ascertained, the four affinities of the carbon atom are *all of equal value.*

These considerations are supported by all our experience, and they render the number of possible carbon compounds very great. For not only can a carbon atom combine with four atoms of one monovalent element, say hydrogen; but it can also unite with two or more elements at the same time: and not only can it be saturated by elements, but wholly or partly by compound radicles, which may themselves be either comparatively simple or complex.

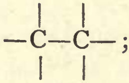
Besides this, the carbon atom also possesses, as above mentioned, an almost unlimited power of linkage with other carbon atoms, to form chains which possess free valencies, that can also be satisfied by monad or polyad elements or by radicles of the same or different types.

But let us consider more fully the manner in which one carbon atom can link or combine with another. If its four valencies are denoted by four points or short lines, the "**bonds**" (C⁞ or C≣), and if it is granted, as facts seem to indicate, that a carbon atom can link itself with other carbon atoms in more than one manner, it can be seen that one atom can link with another in three ways (since it is tetravalent), and yet leave bonds free to combine with other elements or radicles.

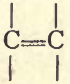
If these facts are expressed graphically, the carbon atom itself and the three different methods of linkage may be represented thus:


$-\overset{|}{\underset{|}{C}}-$;

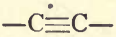
(i.)


$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$;

(ii.)


$\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$;

(iii.)

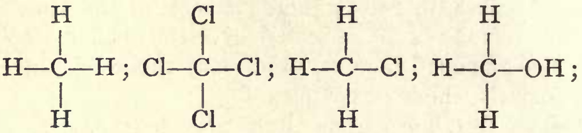

$-C\equiv C-$

(iv.)

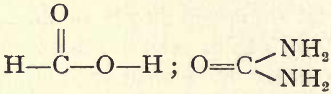
When compounds contain no carbon atoms which are linked to each other by more than one bond, they are termed "**saturated**" compounds; if, however, they contain one or more pairs of atoms linked, as in cases (iii.) and (iv.), they are said to be "**unsaturated.**"

It must, however, be distinctly understood that *the "bonds"* *have no actual existence*, but only serve as a convenient method of indicating graphically on a plane the union in space of atoms which possess volume.

If the different affinities of a single carbon atom are saturated by monad or other radicles, such molecular groups as the following are obtained :—

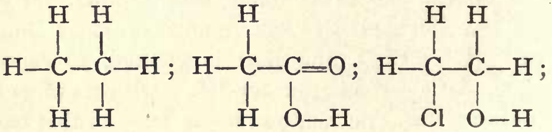


$$H-\overset{H}{\underset{H}{C}}-H\,;\quad Cl-\overset{Cl}{\underset{Cl}{C}}-Cl\,;\quad H-\overset{H}{\underset{H}{C}}-Cl\,;\quad H-\overset{H}{\underset{H}{C}}-OH\,;$$



$$H-\overset{O}{\overset{\|}{C}}-O-H\,;\quad O=C<^{NH_2}_{NH_2}$$

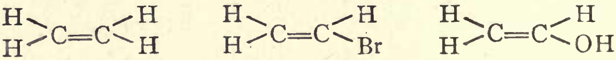
while if two atoms of carbon are bound together by a single linkage, then such compounds as the following can be found :—



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H\,;\quad H-\overset{H}{\underset{H}{C}}-\underset{O-H}{C}=O\,;\quad H-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{O-H}{C}}-H\,;$$

and if more than two atoms are united together, compounds of similar types are obtained.

The unsaturated carbon groups also behave similarly to the saturated; *e.g.* the group $>C=C<$ will give the following compounds amongst others :—

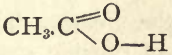


and the group $—C\equiv C—$ yields—

$$H—C\equiv C—H,\quad H—C\equiv C—Br$$

In all such combinations, the sum of the valencies of such atoms or of the radicles combined with one or any number of carbon atoms, must be an *even* number. The necessity of this follows from the tetravalency of the carbon atom, and is known as "Kekulé's law of even numbers."

From these few and simple illustrations, it will be seen that before the constitution of an organic body can be fixed a great many questions must be considered. It is necessary not only to ascertain the empirical formula and the molecular weight of a body; but also to find out both the method in which the carbon atoms themselves are combined, and that in which the other elements are linked to them; *i.e.* to which carbon atom and in what manner they are linked; if the combining elements are monovalent, only the first has to be determined, if polyvalent, both are necessary.

Thus oxygen may be united with a carbon atom directly by both its bonds, or it may at the same time be in union with hydrogen, as in the compound  $CH_3.C\genfrac{}{}{0pt}{}{=O}{\diagdown O-H}$; nitrogen, which is either tri- or penta-valent, may combine in a still greater number of ways, thus: $CH_3.NH_2$, $(CH_3)_2{:}NH$, $(CH_3)_3\vdots N$, HN:C:O, etc.

The manner in which combinations occur may be ascertained, according to circumstances, either by analytical or synthetical methods. The first of these methods may be illustrated by the decompositions which acetic acid undergoes when it is heated with soda-lime or is electrolysed (see pp. 41, 44); the second by the processes by which it is synthesised (see p. 143); or by the synthesis of the paraffin hydrocarbons (pp. 42, 43). Of course these are comparatively simple cases, but the principles are the same as those involved in more complex problems. In fact, the student must earnestly endeavour, throughout the whole of this work, to grasp the facts from which formulæ are deduced.

Carbon compounds are usually divided, for purposes of study, into two groups. The first of these is called the **Fatty or Aliphatic Series,** the members of which can all be derived from the hydrocarbon methane, CH_4; the second is termed the **Aromatic Series,** the simplest member of which is benzene, C_6H_6. Only the fatty series will be studied in the following sections of this work.

SECTION II.

FATTY HYDROCARBONS; HALOID PARAFFINS; MONOHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

CHAPTER VII.

INTRODUCTORY REMARKS.

PERHAPS the greatest difficulty, which the student beginning the study of organic chemistry experiences, arises from the readiness with which compounds of one class may be formed from those of another of which he knows nothing. Before, therefore, studying the typical groups of compounds in detail, it may be helpful to tabulate and indicate the relations of some of them.

The hydrocarbons form the starting-points from which other compounds are derived; and it must be remembered that these readily exchange their hydrogen by suitable means, either directly or indirectly, for other elements, and the residue appears to act as a compound radicle in a series of its compounds.

Take, for example, the hydrocarbon ethane C_2H_6, and note the following compounds which are derivable from it, remembering that other hydrocarbons of the same series yield similarly named derivatives.

DERIVATIVES OF ETHANE, C_2H_6, OR ETHYL HYDRIDE, C_2H_5H.

	Examples.
1. **Halogen Substitution Compounds,** or **Haloid Esters,** are formed by direct replacement of hydrogen in ethane by halogens; or indirectly by the action of phosphorus haloids on the alcohol (hydroxide), *e.g.* $C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$.	Ethyl chloride, or chlor-ethane, C_2H_5Cl. Ethyl bromide, C_2H_5Br, etc.

2. **Alcohols,** the first hydroxyl derivatives of hydrocarbons, are obtained indirectly from halogen compounds; *e.g.* by the typical reaction $C_2H_5I + AgOH = C_2H_5OH + AgI$.	C_2H_5OH, ethyl alcohol.
3. **Ethereal Salts, Compound Ethers,** or **Esters,** are formed either by action of an acid on the alcohol, *e.g.* $C_2H_5OH + H_2SO_4 = \left\{\begin{matrix}C_2H_5\\H\end{matrix}\right> SO_4 + H_2O$; or from halogen compounds and silver or potash salts, *e.g.* $C_2H_5Br + KSH = C_2H_5SH + KBr$.	$C_2H_5SO_4H$, ethyl hydrogen sulphate. $C_2H_5NO_3$, ethyl nitrate. $C_2H_5C_2H_3O_2$, ethyl acetate
4. **Amines** are produced when the radicle ethyl displaces hydrogen in NH_3, *e.g.* by the action of ammonia on a haloid ester, $C_2H_5Br + NH_3 = C_2H_5NH_2 + HBr$.	$C_2H_5NH_2$, ethylamine.
5. **Ethers** are formed by abstraction of a molecule of water from two molecules of an alcohol, *e.g.* $2C_2H_5OH - H_2O = (C_2H_5)_2O$.	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big> O$, ethyl ether.

Alcohols can be oxidised still further, yielding an aldehyde and an acid.

Aldehydes are the first oxidation products of primary alcohols, $2C_2H_5OH + O_2 = 2C_2H_4O + 2H_2O$.	C_2H_4O, acetaldehyde.
Carboxyl Acids are produced when the oxidation of the alcohol is carried further still, $C_2H_5OH + O_2 = C_2H_4O_2 + H_2O$.	$C_2H_4O_2$, acetic acid.

Carbon acids yield a *similar* series of derivatives to those just mentioned, in which it will be seen that the group $CH_3.CO'$, *acetyl,* recurs, just as in the others there is always present the group $C_2H'_5$, *ethyl.*

Thus **Acetic Acid**	$CH_3.CO.OH$
yields **Acetyl or Acetic Chloride;** ...	$CH_3.CO.Cl$
Acetamide	$CH_3.CO.NH_2$
and **Acetic Anhydride,** ... ... or **Acetyl Oxide;**	$\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\Big> O$

METHOD OF STUDY.

The student is strongly advised to first study Sections II. and III., *omitting* all hydrocarbons containing more than two carbon atoms and their derivatives. Then to go through those sections again, mastering the general reactions and properties of the various series of compounds, as well as studying the higher members of such groups. After that the other sections can be taken in turn.

It must also be remembered that the only way in which the student can really learn the subject is by acquainting himself *practically*, not only with the appearance of the compounds or with the tests for recognising them, but with the reactions and methods employed in their production. For this purpose a number of the preparations, processes for which are given, should be undertaken. Those which are marked by a dagger (†) are suitable for such purpose; and the purity of the compounds prepared should be checked, as far as possible, by a determination of their boiling or melting points.

It may also be noted, once for all, that the simple molecular formulæ assigned to the compounds mentioned in this work are usually supported by determinations of their molecular weights; so that, when reasons for assigning constitutional formulæ are discussed, that fact is constantly assumed.

Contractions.—b.p. = boiling point; m.p. = melting point; sp. gr. at $\frac{15^\circ}{4^\circ}$ = specific gravity at 15° compared with water at 4°.

CHAPTER VIII.

SATURATED OR PARAFFIN HYDROCARBONS.

In systematically studying the carbon compounds, it is both most natural and most convenient to commence with the simple compounds of carbon and hydrogen, or **hydrocarbons,** sometimes also termed the **hydrocarbides.**

It is also most natural to start with the saturated hydrocarbons, of which the simplest member is methane, or marsh gas, CH_4. A series of hydrocarbons is formed from this by successive increments of CH_2, because when a hydrogen atom is displaced by the group $—CH_3$, the total increase in the compound is only CH_2. Also if four is the free valency of the first carbon atom, since two valencies are saturated by the carbon atoms themselves for every addition of one carbon atom, the increased valency of a saturated compound will not be four, but two, or the general formula will be C_nH_{2n+2}, where *n* is the number of carbon atoms present.

METHANE OR PARAFFIN SERIES, C_nH_{2n+2}

Methane, CH_4, *marsh gas*, *methyl hydride*, is the first member of the series, and is very widely distributed. It occurs in the gases which escape from the surface of the coal in coal-mines, and since it forms, when mixed with sufficient air, a highly explosive mixture, it renders coal-mining a dangerous occupation, the danger of which can only be overcome by highly efficient ventilation and the use of safety-lamps. It is produced when organic matter decomposes under water, hence the name "marsh gas." Huge quantities of methane, mixed with hydrogen and other hydrocarbons, are given off from the Pennsylvanian oil-springs, and are collected and conveyed in pipes to a distance for use as fuel. It is also evolved from mud volcanoes in Italy, the Crimea, and other places; and, finally, is produced when carbonaceous matter undergoes dry distillation, and is thus present, for example, in large amounts in ordinary coal gas.

(*1) Methane is usually prepared by heating sodium acetate with soda-lime, the reaction being represented by—

$$CH_3.COONa + NaOH = CH_4 + Na_2CO_3$$

Note.—Reactions marked with a star (✳) are types of general reactions.

Process.—A mixture of three parts soda-lime and one part of the acetate is strongly heated in a copper flask or a piece of iron tubing closed at one end, and the gas collected over water in the ordinary manner. A glass vessel may be employed, but is very likely to be cracked if the materials are not dry.

Methane prepared in this manner is always mixed with about 8 per cent. of hydrogen and some ethylene.

(*2) A better way of preparing it is by acting with the zinc-copper couple on a mixture of equal volumes of methyl alcohol and methyl iodide—

$$CH_3I + CH_3.OH + Zn = CH_4 + ZnI(OCH_3)$$

Process.—Dry zinc filings are heated with one-tenth their weight of copper powder (obtained by reducing granulated CuO) till they just become yellow, and some of the couples so formed are introduced into the wide-necked flask fitted with a drop funnel and scrubber tube shown in Fig. 24. The scrubber contains granulated zinc which has been immersed in a solution of copper sulphate, and is fitted with a delivery tube. When a mixture of equal parts of methyl alcohol and methyl iodide is allowed to fall upon the couple, methane is evolved, is freed from vapour of CH_3I by the scrubber, and may be collected in the usual manner.

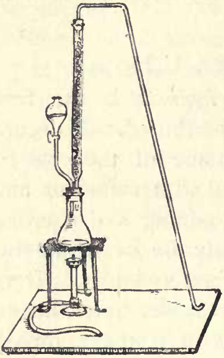


FIG. 24.

Other interesting ways of formation of methane are (*3) its production in a pure condition by decomposing zinc-methyl (p. 180) with water—

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2$$

or (4), when water vapour or H_2S is mixed with CS_2 and passed over heated copper, the following reactions occur:—

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$$
$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO$$

while, finally, (5) when carbon monoxide and hydrogen are subjected to the action of electricity in an induction tube, methane is formed in small quantity.

Reactions No. 4 and No. 5 should be carefully noted, as by means of them the gas can be synthesised from inorganic materials.

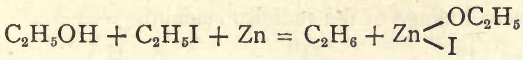
Properties.—Methane is a colourless, odourless gas, slightly soluble in water, more so in alcohol. Its specific gravity is 0·559 (air = 1). It is inflammable, but its flame has very slight illuminating power, the whitish flame usually obtained being due to the traces of ethylene produced during its preparation, from which it can be freed by washing it with strong H_2SO_4. It forms an explosive mixture with air—

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Intense cold and pressure condense it to a liquid of specific gravity 0·415, which boils at −164° (Olszewski). It is decomposed by the passage of an electric spark (see Formation 5), carbon and hydrogen being freed and some acetylene formed. Methane resists the action of HNO_3 and P_2O_5, but a mixture of it and 2 volumes of chlorine exposed to *direct daylight* explodes with the formation of hydrochloric acid and *free carbon;* in diffuse daylight, however, substitution occurs with the production of CH_3Cl, CH_2Cl_2, etc.

Experiment 11.—Prepare methane from sodium acetate, and note (i.) its inflammability ; (ii.) its explosive power when mixed with twice its volume of oxygen or ten times its volume of air.

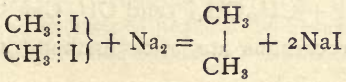
Ethane, $C_2H_6 = CH_3.CH_3$, *Ethyl hydride*, *dimethyl*, the second member of the paraffin series, is found in solution in the crude petroleum of Pennsylvania and in the gases evolved from oil-wells. Ethane can be prepared in a state of purity (*1) by decomposing zinc ethyl with water; but a useful method for ordinary purposes is (*2) the decomposition of ethyl iodide by the Zn-Cu couple in presence of alcohol—



$$C_2H_5OH + C_2H_5I + Zn = C_2H_6 + Zn\begin{matrix}\diagup OC_2H_5\\ \diagdown I\end{matrix}$$

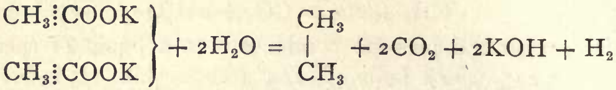
Process.—An apparatus similar to that described for the preparation of CH_4 can be employed, with the addition of scrubbers containing alcoholic soda, bromine water, caustic soda, and lime respectively, in order to free the gas from various impurities, which are absorbed by the reagents named. If, then, a mixture of alcohol and ethyl iodide is added to the Zn-Cu in the flask, and the whole heated to 80°, gas is obtained which after scrubbing contains 98 per cent. ethane and no other combustible gases.

(*3) Another important method for the synthesis of ethane is that in which methyl iodide is treated in ethereal solution with metallic sodium—



$$\left.\begin{matrix}CH_3 \vdots I\\ CH_3 \vdots I\end{matrix}\right\} + Na_2 = \begin{matrix}CH_3\\ |\\ CH_3\end{matrix} + 2NaI$$

while (*4) when potassium acetate is subjected to electrolysis, it decomposes as follows :—



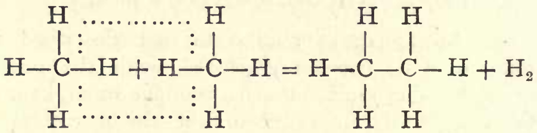
$$\left.\begin{array}{l} CH_3\vdots COOK \\ CH_3\vdots COOK \end{array}\right\} + 2H_2O = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + 2KOH + H_2$$

the C_2H_6 and CO_2 being evolved together at the positive pole. Both the last two methods of formation are important, as they give an important clue to the constitution of ethane.

Properties.—Ethane is an odourless, colourless gas, which is condensible to a liquid at 4°, under a pressure of 46 atmospheres. It is inflammable, and has greater illuminating power than methane. It is almost insoluble in water, but alcohol dissolves 1·5 volumes of the gas. With chlorine in diffuse daylight it forms substitution products.

HOMOLOGY.

We have now studied the properties of two hydrocarbons whose formulæ differ from each other by CH_2. Thus ethane can be looked upon as derived from methane by the substitution of the radicle methyl, CH_3, in place of one of its hydrogen atoms, or as formed from two molecules of methane by the elimination of an atom of hydrogen from each, with subsequent linkage of the radicles remaining—



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} + \begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} = \begin{array}{c} H\quad H \\ |\quad\;\; | \\ H-C-C-H \\ |\quad\;\; | \\ H\quad H \end{array} + H_2$$

and this reaction is indirectly realised by the formation of ethane from methyl iodide and sodium (p. 43).

If, instead of methyl iodide, ethyl iodide, C_2H_5I, is employed, a hydrocarbon *butane*, $C_2H_5.C_2H_5$, is formed; and if a mixture of the two iodides is used, the hydrocarbon *propane*, $CH_3.C_2H_5$, results. That is—

$CH_3.CH_2I + CH_3I$ yield $CH_3.CH_2.CH_3$, and
$CH_3.CH_2.I + CH_3.CH_2I$ yield $CH_3.CH_2.CH_2.CH_3$

These hydrocarbons are, with methane and ethane, the first members of a series of hydrocarbons which differ from each other by $—CH_2—$; and such a series of hydrocarbons, or of their derivatives, is termed a **Homologous Series**, while the individual members are called **Homologues.**

HIGHER MEMBERS OF THE PARAFFIN SERIES.

Among the principal members of the paraffin series are—

Methane,	CH_4	Pentane,	C_5H_{12}
Ethane,	C_2H_6	Hexane,	C_6H_{14}
Propane,	C_3H_8	Heptane,	C_7H_{16}
Butane,	C_4H_{10}	Octane,	C_8H_{18}

The paraffinoid hydrocarbons occur in large quantities in the petroleum which is found in many parts of the world, but notably in North America and Burmah. The deposits of crude paraffin, known as fossil wax and ozokerit, found in Galicia, Roumania, and other places, and the products of the distillation of brown coal and bituminous shale, also yield considerable quantities. Caucasian petroleum contains only small quantities of the paraffins.

Crude petroleum is a mixture of liquid and solid hydrocarbons, and possesses the specific gravity 0·78–0·88, its colour varying from pale yellow or brown to black. Its chemical composition varies very much, and the hydrocarbons present are by no means confined to the methane series; while, besides hydrocarbons, it also contains small quantities of bodies which contain nitrogen and sulphur.

Purification of Crude Petroleum.—To prepare this complex mixture for use it undergoes fractional distillation.

In America two fractions are distilled from the crude oil still, the "benzine" distillate, and that of the "burning oil." The residue is then transferred to another still, where it is distilled till coking takes place; the resulting products yield more burning oils, oils suitable for lubricating purposes, vaseline, and paraffin.

From the "benzine" fraction further distillation separates the following different products: (i.) Cymogene, b.p. 0° C., sp. gr. about 0·600, which is principally butane; (ii.) rhigolene, b.p. 18·3° C., sp. gr. 0·600; (iii.) petroleum ether, b.p. 70–90° C., sp. gr. 0·650–0·666, which consists of pentane and hexane; (iv.) gasoline, b.p. 70–90° C., sp. gr. 0·666–0·690; (v.) naphtha, b.p. 80–110° C., sp. gr. 0·690–0·700; (vi.) ligroine, b.p. 80–120° C., which is mainly heptane and octane, sp. gr. 0·710–0·730; and (vii.) deodorised benzine, b.p. 120–150° C., sp. gr. 0·730–0·750.

Of these bodies the first two are liquefiable by cold or pressure, and find use for producing artificial cold; numbers iii. to vi. are used as solvents in different processes; numbers v. and vi. are used in sponge lamps; while the benzine is used as a substitute for turpentine as a cleansing material.[1]

Both the *benzine* and the *burning oil* from the first distillation are deodorised by treatment with sulphuric acid, followed by washing first with water and then with dilute caustic soda, when the latter oil forms the ordinary petroleum, "kerosene," or mineral sperm.

From the distillate from the tar stills paraffin wax is separated, after washing with acid and soda, by crystallisation from the more liquid hydrocarbons with which it is associated. The more pasty hydrocarbons find employment in the preparation of vaseline, while those between them and the burning oils are used as lubricants.

Since many of these oils evolve combustible vapour at very low temperatures, their use in ordinary lamps would be excessively dangerous. To prevent this danger, it has been enacted in this country that oil whose vapour flashes below 37·8° C. when a light is applied in *open* cups must not be sold for lighting purposes. As many circumstances modify the accuracy of this test, it is now performed in a *closed* tester specially designed by Prof. Abel, in which the **flashing point** is allowed to be 22·7°.

Besides the oily and solid paraffins obtained in quantity from crude petroleum, large quantities of paraffinoid hydrocarbons are present, along with olefines, etc., in the oils obtained by the dry distillation of *paraffin shale*, which is so largely carried on in the south of Scotland. The crude oil is refractionated and deodorised somewhat similarly to the oils from the crude petroleum, with the production of "naphtha," "burning oil" (paraffin oil), "lubricating oils," and "paraffin wax."

From the above-mentioned products, prepared from natural sources, it is possible, by special purification with H_2SO_4 and HNO_3 and subsequent fractional distillation, to prepare pure paraffins; but before considering any of the higher members

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[1] This must not be confounded with the *benzene* obtained from coal-tar oils.

of the series it will be wise to study their general methods of formation and properties.

GENERAL REMARKS ON THE PARAFFINS.

The following reactions which have been illustrated in studying methane and ethane, are general in their application to the preparation of paraffins.

1. Heating the acids of the acetic series with alkalis or alkaline earths. For higher members sodium methylate replaces the alkalis.

2. The action of the Zn-Cu couple on **alkyl**[1] iodides.

3. The decomposition of zinc alkyls by water.

4. The action of metals such as sodium, or reduced silver or zinc at 150° upon alkyl iodides. Sodium is the most convenient, as it acts at a low temperature; it is often necessary to modify the violence of its action by dilution with ether.

5. The electrolysis of the fatty acids.

Besides the above may be mentioned: 6. The reduction of alkyl iodides by such reagents as Zn and H_2SO_4, sodium amalgam, or HI.

Properties.—The members of this group of hydrocarbons are distinguished by their chemical indifference; hence the name "paraffins" which is from the word "paraffin" (*parum affinis*), a term first applied to the white crystalline product obtained by Reichenbach from wood-tar. They are not attacked by KOH, by concentrated H_2SO_4, and hardly by concentrated HNO_3 at ordinary temperatures. If, on the contrary, they are heated with *dilute* HNO_3, H_2CrO_4, or MnO_2 and H_2SO_4 they undergo slow oxidation, CO_2 and H_2O principally resulting, although according to circumstances acids are also formed; strong HNO_3 acts upon the higher members, forming nitro-paraffins. Since they are *saturated* compounds they do not form additive compounds with the haloid acids, and are not absorbed by H_2SO_4 or bromine. Chlorine and bromine act on them, replacing hydrogen and forming haloid

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[1] The term "*alkyl*" or "*alcoholic*" radicle is applied to the residual group of atoms derived from a paraffin hydrocarbon by the loss of *one* atom of hydrogen: thus CH_4 gives CH'_3, C_2H_6 gives $C_2H'_5$.

substitution derivatives, one molecule of the haloid acid being formed for every atom of hydrogen which is thus replaced—

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

The lowest members of the series—methane, ethane, and propane—are gases at 0°, above that to tridecane inclusive they are liquids, and the remainder are solids.

The paraffins are almost or entirely insoluble in water; in alcohol the gases are slightly soluble, the liquids readily so, and the solids little soluble, the solubility decreasing with increase of molecular weight. The specific gravities of the liquid and solid paraffins increase with the molecular weight, but never reach unity. The boiling points of similarly constituted hydrocarbons increase (with each increment of CH_2) by decreasing amounts; until after nonane every increase is about 19° till the limit of temperature is reached at which the hydrocarbons boil under ordinary atmospheric pressure without decomposition.

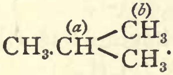
HIGHER PARAFFINS.

Propane, C_3H_8, $CH_3.CH_2.CH_3$, *propyl hydride.*—Propane occurs in crude petroleum. It may be prepared according to Schorlemmer's method by the reduction of normal propyl iodide, or by the action of sodium on a mixture of C_2H_5I and CH_3I.

Properties.—Propane is a colourless gas which at $-25°$ to $-30°$ C. condenses to a liquid, b.p. $-17°$ C. It is inflammable, is slightly soluble in water, more so in alcohol. Chlorine forms both primary and secondary propyl chlorides, $CH_3.CH_2.CH_2Cl$ and $CH_3.CHCl_2$. Its constitutional formula follows from its formation from C_2H_5I and CH_3I, and from the fact that there is only one formula possible if the considerations mentioned on p. 34 are kept in mind.

Paraffins, C_4H_{10}, or **Butanes.**—Although there is only one possible form of the hydrocarbons, CH_4, C_2H_6, and C_3H_8, when we consider those containing four or more carbon atoms, it can be easily shown that those atoms can be linked together in more than one manner; thus there can be *two* compounds with the formula C_4H_{10}, as given on p. 49.

This, then, is the first example of a fact which makes the difficulty of elucidating the constitution of organic bodies much greater, viz. that it is frequently possible for bodies that possess identical percentage composition and the same molecular weight to differ very materially in chemical and physical properties, and so evidently to be very differently constituted. This phenomenon is called **isomerism**, and the substances which differ in this manner are termed **isomers**, or are said to be **isomeric** with each other.

How the two butanes can be formed will be seen if the formula for propane, $CH_3.\overset{(a)}{C}H_2.\overset{(b)}{C}H_3$, is considered. There it will be noted that hydrogen atoms linked to the carbon atoms *a* and *b* evidently bear different relations to the molecule, since *a* is linked to two other carbon atoms, while *b* is attached to only one. Let, then, a hydrogen atom attached to *b* be replaced by CH_3, and the formula for the butane produced is $CH_3.\overset{(a)}{C}H_2.\overset{(b)}{C}H_2.CH_3$. If, on the contrary, an atom attached to *a* is replaced, then the butane is  $CH_3.\overset{(a)}{C}H\begin{smallmatrix}\overset{(b)}{CH_3}\\ CH_3\end{smallmatrix}$. The former is called the **normal (n)**, the latter the **iso** hydrocarbon.

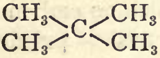
n-Butane, $CH_3.CH_2.CH_2.CH_3$, *butyl hydride, di-ethyl*, occurs in petroleum, and is formed from ethyl iodide by the action of sodium—

$$2CH_3.CH_2 \vdots I + Na_2 = CH_3.CH_2.CH_2.CH_3 + 2NaI$$

hence its formula. It is gaseous at ordinary temperatures, but on cooling forms a liquid, b.p. 1°, sp. gr. 0·6.

Iso-butane, $(CH_3)_3CH$, *tri-methyl-methane*, formed when zinc and water act on tertiary butyl iodide $(CH_3)_3CI$, is a gas which condenses to a liquid, b.p. $-17°$.

Pentanes, C_5H_{12}.—Of the hydrocarbons with this general formula there are *three* isomers—

1. Normal pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$
2. Iso-pentane,  $\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!>CH.CH_2.CH_3$
3. Tetra-methyl-methane,  $\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!>C<\!\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$

n-Pentane is found in petroleum, in resin oil, and in cannel-coal tar. It is a colourless, inflammable liquid, b.p. 37°, sp. gr. 0·633 at $\frac{15^\circ}{15^\circ}$, has an ethereal odour, and is attacked by chlorine with the formation of primary and secondary chlorides.

Iso-pentane occurs in petroleum and cannel-coal tar. It can be formed from iso-amyl iodide or zinc iso-amyl by general methods. It is a mobile liquid, b.p. 30° C., sp. gr. 0·6248 at $\frac{15^\circ}{15^\circ}$. It burns with a brilliant white flame.

Tetra-methyl-methane, obtained from tertiary butyl iodide and zinc methyl—

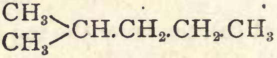
$$2C(CH_3)_3I + Zn(CH_3)_2 = 2C(CH_3)_4 + ZnI_2$$

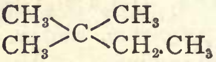
is a colourless liquid, b.p. 9·5°; it can be frozen to a solid, m.p. -20°.

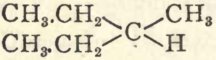
The constitutional formulæ of these substances follow from their methods of formation.

Hexanes, C_6H_{14}.—Of these there are five forms, whose formulæ are—

1. Normal hexane, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$

2. Iso-hexane, 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CH_2.CH_2.CH_3$

3. Tri-methyl-ethyl-methane, 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\!\begin{matrix}CH_3\\CH_2.CH_3\end{matrix}$

4. Methyl-di-ethyl-methane,  ?
$\begin{matrix}CH_3.CH_2\\CH_3.CH_2\end{matrix}\!>C<\!\begin{matrix}CH_3\\H\end{matrix}$

5. Tetra-methyl-ethane, 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CH<\!\begin{matrix}CH_3\\CH_3\end{matrix}$

The number of isomers rapidly increases as the series is ascended, until the number is theoretically almost unlimited. Thus for C_{12} and C_{13} there are theoretically 355 and 802 different forms respectively. It is, however, very doubtful if they would be distinguishable if prepared.

Nomenclature of Paraffins.—If these different groups of hydrocarbons are carefully examined, it will be seen that they can be classified under four heads; viz.—

1. Those in which no carbon atom is linked to more than *two* others, the **normal** or **primary** paraffins, *e.g.* propane.

2. Those which contain one carbon atom linked to *three* other carbon atoms, termed **secondary** or **iso-paraffins,** *e.g.* tri-methyl-methane or iso-butane.

3. There are hydrocarbons which contain a carbon atom linked to *four* others, and it has been proposed to term these **tertiary** or **neo-paraffins,** *e.g.* tetra-methyl-methane, or neo-pentane.

4. When hydrocarbons include *two* carbon atoms *each of which is linked to three others*, these may be termed **meso-paraffins,** *e.g.* tetra-methyl-ethane, or meso-hexane.

This nomenclature has not, however, been generally adopted except for normal and iso-paraffins; but preference has been given to that method which describes a hydrocarbon as being derived from a simpler one by the introduction of some well-known radicle into it. Thus all the normal paraffins can be named as methyl derivatives of the preceding member of the series; and the isomeric paraffins can be similarly treated (see the Pentanes and Hexanes mentioned above). It will be evident that this method has the advantage of indicating clearly the constitution of the hydrocarbon.

CHAPTER IX.

UNSATURATED HYDROCARBONS.

BESIDES the paraffins, which are saturated compounds, there are other series of hydrocarbons which are unsaturated, *i.e.* the number of hydrogen atoms in each member of the series falls short of that which is possible if the carbon atoms are combined to their fullest extent. Only those unsaturated compounds, which differ from the corresponding paraffins by *an even number* of hydrogen atoms, can exist in the free state.

Thus amongst the fatty compounds there are, besides the paraffins, C_nH_{2n+2}, the following unsaturated homologous series: The Olefine or Ethylene series, general formula C_nH_{2n}; the Acetylene or Ethinene series, general formula C_nH_{2n-2}; and besides there are others corresponding to C_nH_{2n-4} and C_nH_{2n-6}, but the above-mentioned are the principal families.

Nomenclature of Hydrocarbons.—Hofmann proposed to distinguish the different families of the hydrocarbons by their terminology. The first series to have names ending in **-ane**, the second in **-ene**, the third in **-ine**, and so on; *e.g.* C_2H_6 is ethane, C_2H_4 is ethene, and C_2H_2 is ethine. Although this nomenclature possesses certain advantages, it has not been generally adopted; and it is proposed to follow in this work the method adopted in Watts' "Dictionary" (new edit.), and to give names ending in **-ene** to **all unsaturated hydrocarbons**, while distinguishing each series by the use of a significant letter before such ending.

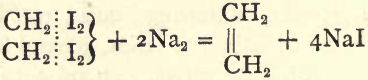
Thus the names of the hydrocarbons C_nH_{2n} end in **-ylene**; C_nH_{2n-2} in **-inene**, and so forth.

Unsaturated combinations of hydrogen and carbon, the valency of which is an odd number, cannot exist free, and are given names derived from those of the hydrocarbons and ending in the syllable **-yl**; *e.g.* methane yields methyl, ethane ethyl, etc.

OLEFINES OR ALKYLENES, C_nH_{2n}.

Ethylene,	C_2H_4	Hexylene,	C_6H_{12}
Propylene,	C_3H_6	Heptylene,	C_7H_{14}
Butylene,	C_4H_8	Octylene,	C_8H_{16}, etc.
Amylene,	C_5H_{10}		

It might have been expected that this series of hydrocarbons, **isologous**[1] with those of the methane series, would have included methylene, CH_2, corresponding to methane in the same way that ethylene does to ethane; but hitherto all attempts to prepare it have utterly failed. Thus when di-iodo-methane is treated with sodium, or methyl chloride with potash, ethylene, and not methylene, is produced.



$$\left.\begin{array}{l} CH_2\vdots I_2 \\ CH_2\vdots I_2 \end{array}\right\} + 2Na_2 = \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + 4NaI$$

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[1] An isologous series is one in which the members differ from each other by H_2; *e.g.* C_2H_6 and C_2H_4 are isologous.

$$\text{and} \left.\begin{array}{l}CH_2\vdots HCl\\ CH_2\vdots HCl\end{array}\right\} + 2KOH = C_2H_4 + 2KCl + 2\,H_2O$$

Ethylene or **Ethene**, $CH_2{=}CH_2$, *olefiant gas.*—Since methylene, CH_2, cannot exist, this is the first of the olefines to be considered. It occurs in coal gas, of which it is an important illuminating constituent, and is a product of the dry distillation of many organic bodies.

(*1) It is produced when ordinary alcohol, C_2H_5OH, is heated with concentrated H_2SO_4 to about 165°; water is eliminated and ethylene is evolved. The reaction probably occurs in two stages—

$$\text{(i.)}\quad C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5SO_4H} + H_2O$$

$$\text{(ii.)}\quad C_2H_5SO_4H = C_2H_4 + H_2SO_4$$

† *Process.*—Mix 25 grams of absolute alcohol with 150 grams conc. H_2SO_4, place in 2–3 litre flask (Fig. 25), and heat upon a sand-bath till the gas is rapidly evolved, which takes place at about 165°.

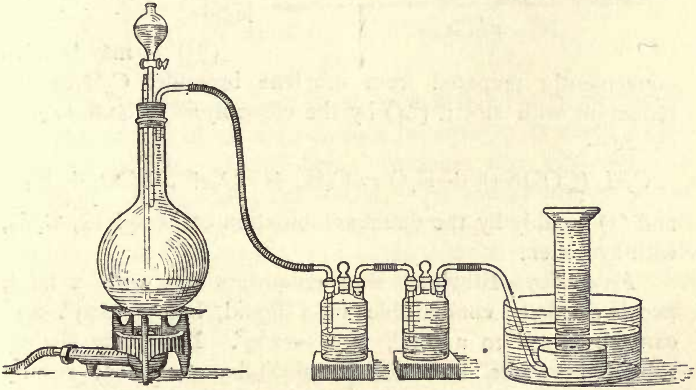


FIG. 25.

Then run in slowly a mixture of 2 parts H_2SO_4 and 1 part alcohol. Wash the gas first with conc. H_2SO_4 and then with NaOH, and collect over water. The addition of sand to the mixture, or of a thin layer of paraffin oil, tends to prevent frothing.

(*2) Another important method of producing ethylene is by heating ethyl iodide, C_2H_5I, with alcoholic potash, when HI is withdrawn and ethylene evolved—

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O$$

Process.—The apparatus shown in Fig. 26 may be employed. It consists of a small flask provided with a drop funnel and reflux condenser, which latter is in turn connected with another flask fitted with a reflux condenser and an exit tube. Alcoholic potash is placed in both flasks and boiled, while C_2H_5I is dropped in from the funnel. The condensers prevent loss of alcohol, and the second flask ensures the complete decomposition of the iodide.

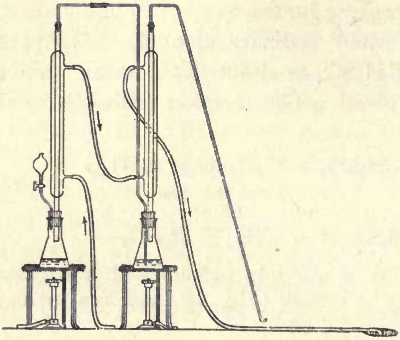


FIG. 26.

(*3) It may be also conveniently prepared from ethylene bromide, $C_2H_4Br_2$, by reduction with zinc; (*4) by the electrolysis of sodium succinate—

$$C_2H_4 (COONa)_2 + H_2O = C_2H_4 + CO_2 + Na_2CO_3 + H_2$$

and (5) notably by the direct combination of acetylene, C_2H_2, with hydrogen.

Properties.—Ethylene is a colourless gas with a faint, peculiar odour, condensible to a liquid, b.p. $-103°$, and can be frozen to a solid, m.p. $-169°$. It is very slightly soluble in water, more so in alcohol and ether; readily inflammable, and burns with a luminous flame. It forms an explosive mixture with air or oxygen, and when brought into contact with ozonised oxygen spontaneously explodes. A mixture of ethylene and chlorine burns, when ignited, with a smoky flame, forming HCl and free carbon. Ethylene in alcoholic solution readily combines with Cl_2, Br_2 or I_2—

$$C_2H_4 + Cl_2 = \underset{\text{Ethylene dichloride}}{C_2H_4Cl_2}$$

It also unites with HI and HBr, but *not with HCl*—

$$C_2H_4 + HI = C_2H_5I\,;$$

and an aqueous solution of HOCl forms *ethylene chlorhydrin*—

$$CH_2 = CH_2 + HOCl = CH_2Cl.CH_2OH$$

It dissolves in strong H_2SO_4 to form ethyl hydrogen sulphate, $C_2H_5SO_4H$, and in presence of platinum black unites with hydrogen to form ethane. Ethylene is oxidised by HNO_3 to glycol, and by other oxidising agents to glycol, and oxalic and formic acids.

Experiment 12.—Prepare ethylene by the first method, note its inflammability, its explosive power when mixed with 3 volumes of oxygen, and the oily compound produced on mixing it with its own volume of chlorine.

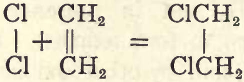
Constitution of Ethylene.—Ethylene can only have one of three formulæ, viz.—

$$\underset{\text{(i.)}}{CH_3.CH=}\,,\quad \underset{\text{(ii.)}}{\overset{|}{C}H_2.\overset{|}{C}H_2}\,,\ \text{and}\ \underset{\text{(iii.)}}{CH_2{=}CH_2}$$

The first two of these three are rendered very improbable by the failure of all experiments hitherto to produce hydrocarbon radicles of any sort possessing *free* valencies; *e.g.* neither $—CH_3$, C_2H_5, nor $—CH_2—$ have ever been obtained in the free condition, but reactions expected to yield them always give C_2H_6, C_4H_{10}, and C_2H_4 respectively. It is more in accordance, too, with the tetravalent behaviour of carbon that the "bonds" should be saturated, if not by other elements, by carbon itself.

There is, however, more positive evidence which can be adduced in favour of a symmetrical formula for ethylene, as opposed to that first given. Its formation from methylene iodide or methyl chloride is most readily explicable on the assumption that $=CH_2$ is freed and unites to form ethylene, $H_2C = CH_2$; and its production from succinic acid by electrolysis also supports the same conclusion.

Besides this, ethylene combines with chlorine to form a compound $C_2H_4Cl_2$; now, the formula of ethane, $CH_3.CH_3$, would lead us to expect *two* possible compounds of that general formula, viz. $CH_3.CHCl_2$ and $CH_2Cl.CH_2Cl$. It will be shown later (p. 73) that that which is formed by the addition of chlorine to ethylene has probably the second of these formulæ; and its formation is most easily understood on the assumption that a reaction such as the following occurs:—



$$\begin{array}{c} Cl \\ | \\ Cl \end{array} + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} = \begin{array}{c} ClCH_2 \\ | \\ ClCH_2 \end{array}$$

or that the ethylene molecule is symmetrical.

GENERAL REMARKS ON THE OLEFINES.

Ethylene has furnished us with several methods which are of general value in the formation of olefines. Thus they are obtained—

1. By the abstraction of the elements of water from alcohols. The use of conc. H_2SO_4 for this purpose has been illustrated and explained. Frequently $ZnCl_2$ or P_2O_5 may be advantageously employed, and in some cases the higher alcohols yield olefines by mere application of heat.

2. By elimination of HCl, HBr, or HI from haloid paraffins by heating with alcoholic KOH. In some cases the vapour must be passed over heated CaO or PbO, and in others simple distillation of the chlor-paraffin suffices to yield them.

3. By electrolysis of the alkaline salts of acids of the succinic series.

4. By the action of metals upon di-haloid paraffins, *e.g.* upon $C_2H_4Cl_2$.

5. Besides the above-named methods, olefines are produced in the destructive distillation of many organic substances.

Properties.—In physical properties the olefines closely resemble the paraffins. At the ordinary temperature the lower members of the series are gaseous, up to hexadecylene they are liquid, and above that they are solid. They burn with luminous flames, which become more smoky as the molecular weight of the hydrocarbons increases. Their specific gravities lie between about 0·63 and 0·80; their boiling points are very near to those of the corresponding paraffins, but their melting points are much lower than theirs.

In chemical properties the olefines differ from the paraffins in a striking manner, on account of being unsaturated compounds. Many of their reactions have already been illustrated in studying ethylene. They unite directly with the halogens, the halogen acids, and with hypochlorous acid to form respectively di-haloid and mono-haloid hydrocarbons and the so-called "chlorhydrins," although all do not combine with equal readiness. Olefines are more or less readily absorbed by strong H_2SO_4, with the formation of acid sulphates. These salts, when boiled with water, become hydrolysed,[1] and yield the acid and an alcohol—

$$\underset{\text{Iso-propyl hydrogen sulphate}}{CH_3.CH(SO_4H).CH_3} + H_2O = \underset{\text{Iso-propyl alcohol}}{CH_3.CH(OH).CH_3} + H_2SO_4$$

It may be noted that in most cases when these acids combine with the olefines, the acid radicle attaches itself to the least hydrogenised carbon atom, of which general law the combination of propylene with sulphuric acid is an example.

The oxidation products of olefines differ with the oxidising agents employed, rupture of the double bond usually occurring. The olefines readily polymerise in presence of strong H_2SO_4, $ZnCl_2$, BF_3, etc., *i.e.* form **polymers**, which are substances of the same percentage composition, but different molecular weight. Ethylene is an exception to this rule.

Propylene, $CH_3.CH:CH_2$, *propene, methyl-ethylene.*—This gas occurs in coal-gas, and is a frequent product of the decomposition of organic bodies by heat; thus it is produced when the vapour of amyl alcohol is passed through a red-hot tube. Propylene may be produced in a pure state either (1) from iso-propyl alcohol, $CH_3.CH(OH).CH_3$, or (2) from the propyl iodides. Also it is formed (3) when allyl iodide, C_3H_5I, is reduced by pure zinc in alcoholic solution.

Properties.—Propylene is a gas with a garlic-like odour; it is liquefiable by pressure to a liquid. It is moderately soluble

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[1] "Hydrolysis" is a term used to express the taking up of the elements of water by ethers or esters with resolution into two molecules of an alcohol, or into a molecule of an alcohol and an acid. The latter case is very frequently distinguished as "saponification."

in alcohol, and readily in H_2SO_4, forming iso-propyl hydrogen sulphate. It combines readily with the halogens and the halogen hydrides, and easily undergoes polymerisation.

Butylenes, C_4H_8.—There are three isomeric hydrocarbons of this formula. All are known, and all occur in the oils from compressed coal-gas. They are: (1) **Normal** or α-**butylene,** $CH_3.CH_2.CH{:}CH_2$, obtained from n-butyl iodide, $CH_3.CH_2.CH_2.CH_2I$, by KOH, is a gas condensible to a liquid, b.p. $-4°$; (2) ψ or β-**butylene,** $CH_3.CH{:}CH.CH_3$, obtained by the action of KOH on secondary butyl iodide, $CH_3.CH_2.CHI.CH_3$, is a gas which forms a liquid, b.p. 1°, sp. gr. 0·635; and (3) **Iso-butylene,** $(CH_3)_2{:}C{:}CH_2$, which can be obtained from tertiary butyl iodide, $(CH_3)_3CI$, is an unpleasant-smelling gas, which yields a liquid, b.p. $-6°$, sp. gr. 0·637 at $\frac{-14°}{4°}$. From its solution in H_2SO_4, tertiary butyl alcohol is formed on boiling with water.

Of the **amylenes** or **pentylenes,** C_5H_{10}, five isomeric forms might be expected, and five are known. Two of these are found in quantity along with a trace of a third in—

"**Iso-amylene,**" or commercial amylene, which is obtained when $ZnCl_2$ is distilled with iso-amyl alcohol (p. 101). The distillate boils at 25–40°, and contains 90 per cent. tri-methyl-ethylene, 10 per cent. methyl-ethyl-ethylene, and a trace of iso-propyl-ethylene.

The amylenes are the following:—(1) α-**amylene** or **n-pentylene,** $CH_3.CH_2.CH_2.CH{:}CH_2$, has not been obtained pure; it is a liquid, b.p. about 40°; (2) **iso-amylene** or **iso-pentylene,** $(CH_3)_2{:}CH.CH{:}CH_2$, found in commercial amylene in small quantity, is a fragrant liquid, b.p. 21·1°; (3) β-**amylene,** $CH_3.CH{:}CH.CH_2.CH_3$, found in commercial amylene, and also formed from α-amyl iodide, is a liquid, b.p. 36°; (4) γ-**amylene,** $CH_3.CH_2.C.(CH_3){:}CH_2$, found in Alsatian petroleum, and obtained from active amyl iodide, is a liquid, b.p. 32°; while (5) **tri-methyl-ethylene,** $(CH_3)_2{:}C{:}CH.CH_3$, forms 90 per cent. of commercial amylene. It is a liquid, b.p. 36°, and polymerised by $ZnCl_2$ or H_2SO_4 to di-amylene.

CHAPTER X.

UNSATURATED HYDROCARBONS—Continued.

HYDROCARBONS OF THE ACETYLENE SERIES, C_nH_{2n-2}.—

Acetylene, ethine, or ethinene,	C_2H_2
Allylene or propinene,	C_3H_4
Crotonylene or butinene,	C_4H_6
Valerylene or pentinene,	C_5H_8, etc.

The first member of this series does not permit, according to our present ideas on the linkage of atoms, of more than one constitutional formula, but two modifications are possible in the case of allylene, and the isomers increase in number as the series ascends. The hydrocarbons of this group may be classed under three heads :—

1. Those which contain two carbon atoms linked together by *three* bonds. Of these acetylene, $HC{\equiv}CH$, is the simplest instance; and there are producible from this two varieties of derivatives: (i.) those which are unsymmetrical and correspond to the type $R'C{\equiv}CH$, *e.g.* allylene, $CH_3.C\vdots CH$, and which are "**true acetylenes,**" because they contain the group $—C{\equiv}CH$; and (ii.) the symmetrical derivatives, of which $R'C{\equiv}CR'$ is the general formula, *e.g.* crotonylene, $CH_3.C\vdots C.CH_3$.

2. There are hydrocarbons which contain a tetravalent triad of carbon atoms, one of which is united to each of the other two atoms by two bonds, $=C=C=C=$; of this class allene, $H_2C=C=CH_2$, is the first example.

3. There are, finally, hydrocarbons that may be termed di-ethylenic, and contain two groups, $=C=C=$, of which diallyl, $H_2C=CH.CH_2.CH_2.HC=CH_2$, is an illustration.

Acetylene, $CH\vdots CH$, *ethine* or *ethinene*, is found in coal gas. It is formed—(1) By the direct union of hydrogen and carbon when a powerful electric current is passed from carbon poles through an atmosphere of hydrogen, as in Fig. 27. The hydrogen passes in at H, and the stream of gases is passed over an ammoniacal solution of cuprous chloride[1] contained in the flask, where red copper acetylide is formed—

$$Cu_2Cl_2.2NH_3 + H_2O + C_2H_2 = 2NH_4Cl + C_2Cu_2H_2O$$

A little sand at the bottom of the globe prevents it being cracked by pieces of red-hot charcoal from the poles.

(*2) Acetylene is also readily prepared by the action of alcoholic potash upon di-brom-ethane or brom-ethylene. In the latter case—

$$CH_2{:}CHBr + KOH = CH{\vdots}CH + KBr + H_2O$$

This is quite similar in principle to the preparation of an olefine from a bromo- or iodo-paraffin (see Ethylene, p. 54).

Process.—Employ the apparatus shown in Fig. 26, p. 54 (for small quantities the simpler arrangement shown in Fig. 28), and collect the gas over water; or form from it the red copper compound.

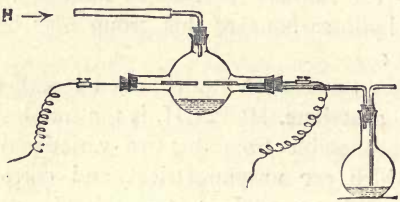


FIG. 27.

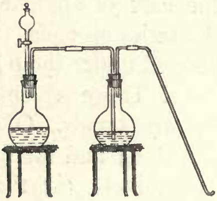


FIG. 28.

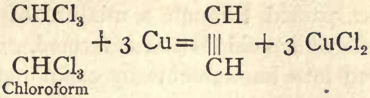
(*3) It is yielded by the electrolysis of sodium fumarate or maleate—

$$\begin{array}{l:l} CH & COOH \\ \| & \\ CH & COOH \end{array} = \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2 + H_2$$

This, again, is analogous to the formation of ethylene from succinic acid (*q.v.*); while (4) it can be produced from chloroform, bromoform, or iodoform by decomposing them with such metals as copper, silver, or zinc—

---

[1] Cuprous chloride is best prepared by dissolving CuO in cold HCl, pouring the solution on copper turnings, and, when it is decolourised, almost neutralising it by well-cooled strong ammonia, and finally making alkaline with it.



$$\begin{matrix} CHCl_3 \\ CHCl_3 \end{matrix} + 3\,Cu = \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 3\,CuCl_2$$

Chloroform

a reaction analogous to the production of ethylene from CH_2I_2 (p. 52), or of ethane from CH_3I (p. 43).

5. Acetylene is formed in considerable quantities during the incomplete combustion of coal-gas, as, for example, when a Bunsen burner burns only at the bottom.

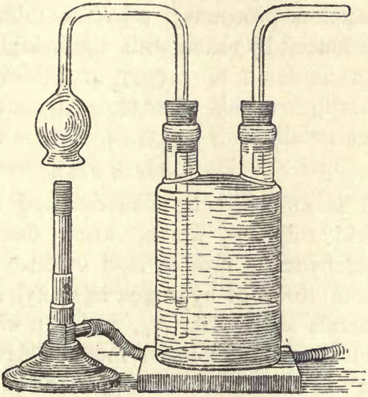


FIG. 29.

Process.—Allow a Bunsen burner to burn back, and draw the products of incomplete combustion by means of an aspirator through ammoniacal cuprous chloride (Fig. 29). The red copper compound is formed, and, after washing, the acetylene may be liberated from it by means of HCl.

Finally (6), the gas is readily prepared, and in a remarkably pure condition, by the action of barium or of calcium carbide[1] upon water.

$$BaC_2 + 2H_2O = C_2H_2 + Ba(OH)_2$$

Properties.—Acetylene is a colourless gas with a very disagreeable and characteristic odour; it is poisonous, burns with a smoky flame, and is condensible to a mobile refractive liquid whose sp. gr. is 0·451 at 0°. In presence of platinum black, it unites with hydrogen to form successively ethylene and ethane (see Ethylene, p. 55). It forms a very explosive mixture with 2½ volumes of oxygen. When an induction spark is passed through it, it is decomposed with separation of carbon; this is remarkable, seeing that it is formed by the union of its elements under the influence of the electric arc. If, however,

---

[1] Prepared by igniting barium carbonate, magnesium, and carbon together—

$$BaCO_3 + 3Mg + C = BaC_2 + 3MgO$$

the sparks are passed through a mixture of nitrogen and acetylene, hydrocyanic acid, HCN, is formed. Acetylene can also be resolved into its elements by exploding a percussion cap in it; and it readily polymerises on passing through heated tubes, with the formation of benzene, C_6H_6, styrene, C_8H_8, and other hydrocarbons. Being unsaturated, acetylene unites with the halogens and with the haloid hydrides, to form substituted olefines or paraffins according to the stage to which the reaction proceeds; *ethylidene* derivatives being ultimately produced by union with the haloid acids (see pp. 71, 72).

$$C_2H_2 + Br_2 = C_2H_2Br_2$$
$$C_2H_2 + Br_4 = C_2H_2Br_4$$
$$C_2H_2 + HBr = CH_2{:}CHBr$$
$$C_2H_2 + 2HBr = CH_3.CHBr_2$$

It is absorbed by concentrated sulphuric acid, forming an acid sulphate, which, when decomposed by water, yields aldehyde. Chromic acid oxidises it to acetic acid. One or both atoms of hydrogen in acetylene can be replaced by such metals as Na, K, Ag, and Cu, with the formation of highly unstable and explosive metallic derivatives; of these the silver salt is white, and the copper salt red.

GENERAL REMARKS ON THE ACETYLENES.

The following methods, which are general in their application to the hydrocarbons of the Acetylene series, have been illustrated in the case of acetylene:—

1. Acetylenes are formed when di-haloid paraffins or mono-haloid olefines are treated with alcoholic potash.

2. They are formed when unsaturated dibasic acids of the fumaric series (p. 241) undergo electrolysis. Besides these synthetical processes, they often result along with other hydrocarbons as the product of the dry distillation of organic substances.

The student should again specially note the analogy of the two methods given to those which are employed in preparing olefines.

Properties.—Since the hydrocarbons possess four unsaturated affinities, they can combine with either one or two molecules of a halogen, or of a haloid acid. In the first case, ethylenic substitution products are formed; in the second, true fatty compounds. They can also combine with hydrogen to form olefines or paraffins.

Those which have been termed "true acetylenes" possess one very characteristic property. The triple linkage of the carbon atoms renders the hydrogen atoms very negative or acid in their character, so that in the case of acetylene two hydrogen atoms, and in substituted acetylenes of the type $R'C \equiv CH$ one hydrogen atom, are replaceable by metals. Thus the true acetylenes form precipitates in ammoniacal silver nitrate or cuprous chloride solutions, the precipitate which is formed being decomposed by acids, with liberation of the hydrocarbons. They also give precipitates with $HgCl_2$, which, when treated with acids, yield derivatives of aldehydes or ketones.

They are slowly absorbed by concentrated sulphuric acid, and the compounds formed on distillation with water yield aldehydes or ketones (difference from olefines). Several of the acetylenes also undergo polymerisation by heat or other agent with great facility, forming aromatic hydrocarbons. Very many of these properties have already received ample illustration in the case of acetylene itself.

Of the higher hydrocarbons mention may be made of allylene, allene, and crotonylene.

Allylene, $CH_3.C\vdots CH$, *propinene*, *methyl-acetylene*, is formed from (1) propylene bromide, $CH_3.CHBr.CH_2Br$, and chloro- or bromo-propylene, $CH_3.CH:CHBr$; and (2) citraconic or mesaconic acids, $C_3H_4(COOH)_2$, by the methods indicated above. It is a colourless gas with a disagreeable odour, burns with a smoky flame, and is similar to acetylene in its properties, forming metallic derivatives, in which, however, only *one* hydrogen atom is replaceable by a metal. Its solution in sulphuric acid when distilled with water yields tri-methyl benzene, C_9H_{12}.

Allene, $H_2C:C:CH_2$, *iso-allylene*, isomeric with the last body, is formed in the electrolysis of potassium itaconate and from the di-chlor-propylene, $CHCl:CH.CH_2Cl$. It is a gas which smells like allylene, and *does not* give a precipitate with ammoniacal silver or copper solutions.

Crotonylene, $CH_3.C\vdots C.CH_3$, *butinene*, *di-methyl-di-acetylene*, from butylene bromide, is a liquid with a pungent odour, b.p. 18°. Shaken with H_2SO_4 diluted with $\frac{1}{3}$ part of water, it polymerises to solid hexamethyl-benzene, $C_{12}H_{18}$. The syntheses of benzene derivatives from acetylenes are specially noteworthy.

CHAPTER XI.

HALOGEN SUBSTITUTION DERIVATIVES OF THE PARAFFINS.

By **substitution** derivatives are meant compounds formed by replacing an element, or group of elements, in a compound, by some other element or radicle.

The halogen derivatives of the paraffins may be prepared as a rule by one or other of the following reactions:—

1. By the direct action of halogens upon hydrocarbons. Many compounds containing chlorine can be so prepared, a molecule of hydrochloric acid being formed for every atom of chlorine introduced. Thus—

$$CH_4 + Cl_2 = CH_3Cl + HCl$$
$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

This action is not so simple as it appears, since in the preparation of the lower substitution products a *mixture* of mono- and poly-haloid compounds always results. Thus if equal volumes of chlorine and methane act on each other, as in the equation given, other chlorinated bodies are formed besides mono-chlormethane, and a certain amount of unchanged methane remains.

In the case of higher hydrocarbons, this further action may be partially avoided by allowing the vapour only to react with the halogen; then, since the chloro-derivative boils at a higher temperature than the hydrocarbon, it condenses as it forms, and is thus removed from the sphere of action. The action of chlorine upon hydrocarbons is very much accelerated by the action of light, and also by the presence (in liquid hydrocarbons) of a little iodine dissolved in them. This latter action depends upon the preliminary formation of ICl_3. Amongst other substances which act as chlorine-carriers may be mentioned $SbCl_5$ and $FeCl_3$. As light aids the action of chlorine, so heat assists that of bromine, but iodine substitutes with more difficulty than either chlorine or bromine; for when it acts alone, the hydriodic acid which is produced at the same time reacts upon the iodo-derivative, and once more produces the hydrocarbon. If, however, HgO or HIO_3 is used along with the iodine, it will react upon the HI formed, and thus prevent its reducing action. Their action may be represented—

$$HgO + 2HI = HgI_2 + H_2O$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O$$

2. Another very important method for producing these compounds depends upon the action of the haloid acids, or haloid phosphorus compounds, upon the corresponding alcohols; *e.g.*—

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl = \underset{\text{Ethyl chloride}}{C_2H_5Cl} + HOH$$
$$\underset{\text{Methyl alcohol}}{CH_3OH} + PCl_5 = \underset{\text{Methyl chloride}}{CH_3Cl} + POCl_3 + HCl$$
$$3CH_3OH + POCl_3 = 3CH_3Cl + PO(OH)_3$$
$$3CH_3OH + PCl_3 = 3CH_3Cl + P(OH)_3$$

In the first case the reaction is never complete; it depends in part upon the relative masses of the two reacting substances, in part upon the temperature at which they react. It is analogous to the formation of metallic salts from hydroxides (compare "Constitution of Alcohols," pp. 83, 96), and is an example of "esterification," which is more fully discussed in dealing with the formation of ethereal salts, or "esters" (p. 119). Of the three haloid acids, HI acts with the most readiness.

The phosphorus haloid compounds are the most generally useful, but the phosphoric and phosphorous acids formed in the last two reactions react with the alcohols to form salts, so that there is always considerable loss of alcohol.

To prepare the bromides and iodides it is customary to use phosphorus and bromine, and phosphorus and iodine respectively, instead of the ready-prepared phosphorus compounds, *e.g.*—

$$3CH_3OH + P + Br_3 = 3CH_3Br + P(OH)_3$$
$$5CH_3OH + P + I_5 = 5CH_3I + PO(OH)_3 + H_2O$$

In studying these compounds the chlorine derivatives will be taken first, then the bromine, and finally the iodine compounds, grouped as shown below:—

	Chlorine derivatives.	Bromine derivatives.	Iodine derivatives.
1	Methyl chloride, CH_3Cl Ethyl ,, C_2H_5Cl	Methyl bromide, CH_3Br Ethyl ,, C_2H_5Br	Methyl iodide, CH_3I Ethyl ,, C_2H_5I
2	Methylene chloride, CH_2Cl_2 Ethylene ,, Ethylidene ,, } $C_2H_4Cl_2$	Methylene bromide, CH_2Br_2 Ethylene ,, Ethylidene ,, } $C_2H_4Br_2$	Methylene iodide, CH_2I_2 Ethylene ,, Ethylidene ,, } $C_2H_4I_2$
3	Chloroform, $CHCl_3$	Bromoform, $CHBr_3$	Iodoform, CHI_3
4	Carbon tetra-chloride, CCl_4	Carbon tetra-bromide, CBr_4	Carbon tetra-iodide, CI_4

This grouping enables compounds of like type to be taken together, and the student should carefully compare not only those connected together in the vertical column, but also those which occur in the same horizontal line.

GROUP I.—MONO-HALOGEN DERIVATIVES.

Methyl Chloride, CH_3Cl, *chlor-methane.*—The formation of methyl chloride (1) from CH_4 and Cl_2, and (2) from methyl alcohol and HCl, have been mentioned already (pp. 64, 65).

Process.—The latter reaction may be carried out either (i.) by heating methyl alcohol (1 part) with salt (2 parts) and sulphuric acid (3 parts); or (ii.) by passing gaseous HCl into a boiling mixture of 1 part fused $ZnCl_2$ and 2 parts CH_3OH contained in a flask provided with a reversed condenser, which method yields it in a pure state.

(3) It is produced on a large scale by neutralising the tri-methylamine, obtained in the distillation of beet-root "vinasse," with hydrochloric acid, and distilling the salt at 260°.

$$\underset{\substack{\text{Tri-methylamine}\\\text{hydrochloride}}}{3N(CH_3)_3HCl} = \underset{\substack{\text{Methyl}\\\text{chloride}}}{2CH_3Cl} + \underset{\text{Tri-methylamine}}{2N(CH_3)_3} + \underset{\text{Methylamine}}{CH_3NH_2} + HCl$$

Properties.—It is a colourless gas with ethereal odour, burns with a green-edged flame, is condensible by pressure to a liquid, b.p. $-23\cdot7^\circ$, sp. gr. $0\cdot991$ at $\frac{23\cdot7^\circ}{\cdot}$, is little soluble in water, more so in alcohol, forms a crystalline hydrate with water at $-7\cdot3^\circ$, and its neutral solution gives no precipitate with $AgNO_3$, thus differing in a marked manner from its analogue KCl. It yields methyl alcohol when heated under pressure with water or dilute KOH—

$$CH_3Cl + H_2O = CH_3OH + HCl$$

It is used in a compressed condition for producing intense cold, and also in the manufacture of artificial colouring matters.

Ethyl Chloride, $CH_3.CH_2Cl$, *chlor-ethane.*—This substance can be formed quite similarly to methyl chloride, (1) by direct chlorination of ethane, (2) by the action of PCl_5 upon ethyl alcohol, and (3) by the action of HCl upon the alcohol alone or, most conveniently, in presence of $ZnCl_2$ (see reactions above, p. 65).

†*Process.*—Dissolve 150 grams $ZnCl_2$ in 300 grams 95 per cent. alcohol; boil the mixture in a flask provided with an inverted condenser and delivery tube (arranged for example as in Fig. 39), and pass gaseous HCl through it. The gaseous product is then washed through KOH solution and either dissolved in alcohol, or else condensed by cold to a liquid and sealed up in tubes. It can also be prepared by distilling together 5 parts alcohol, 2 parts H_2SO_4, and 12 parts NaCl.

Properties.—Below $12\cdot5^\circ$ ethyl chloride is a colourless, mobile liquid, with an ethereal odour and a burning taste, sp. gr. $0\cdot923$ at $\frac{2^\circ}{2^\circ}$. It burns with a green-edged flame, is little soluble in water, but readily in alcohol. It gives no precipitate with $AgNO_3$ in the cold; on heating however, in aqueous or alcoholic solution, a precipitate of AgCl is obtained. It yields alcohol when heated with water, or dilute KOH, under pressure; and when heated with soda-lime, marsh gas and hydrogen are obtained.

Methyl Bromide, CH_3Br, *bromo-methane.*—It has been already pointed out that the bromine derivatives are readily prepared by acting upon the corresponding alcohol with phosphorus and bromine; and methyl bromide is formed thus from methyl alcohol.

Process.—Heat a well-cooled mixture of 6 parts methyl alcohol, 1 part phosphorus, with 6 parts of bromine; wash the evolved gas through KOH, and condense it in a vessel surrounded by a freezing mixture.

Properties.—Methyl bromide is thus obtained as a colourless mobile liquid, somewhat resembling chloroform, b.p. 4·5°, sp. gr. 1·73 at $\frac{0^\circ}{0^\circ}$, which burns difficultly with a greenish-brown flame.

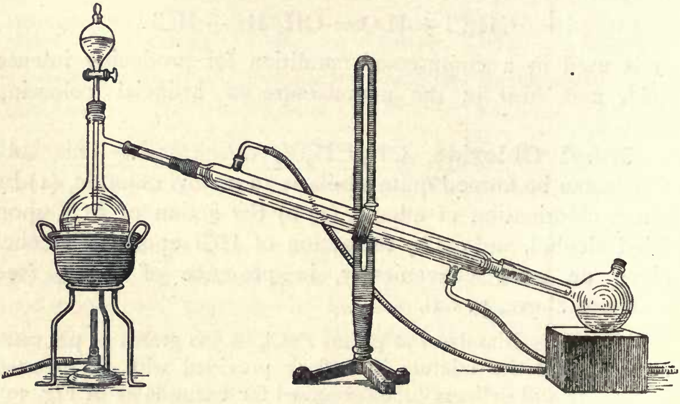


Fig. 30.

Ethyl Bromide, $CH_3.CH_2Br$, *brom-ethane*, is formed by the action of phosphorus and bromine upon ethyl alcohol—

$$3C_2H_5OH + P + Br_3 = 3C_2H_5Br + H_3PO_3$$

†*Process.*—Mix together in a ½-litre distilling flask connected with condenser and receiver (Fig. 30), 13·3 grams of red phosphorus, and 80 grams of *absolute* alcohol. Add to this slowly from the

dropping-funnel 80 grams of bromine, cooling if necessary. Allow to stand two or three hours, and then distil from the water-bath. Wash the distillate in a separating funnel, first with weak NaOH, then three times with water. Dehydrate over $CaCl_2$ or K_2CO_3 and distil, collecting that apart which boils between 36° and 40°. This can be further rectified if required, by redistillation.

Properties.—Ethyl bromide is a colourless liquid similar to the chloride in taste and smell. Its b.p. is 38·4°, and sp. gr. at $\frac{15°}{4°}$ is 1·4189. It burns with a green *smokeless* flame with evolution of bromine, and is employed as an anæsthetic.

Methyl Iodide, CH_3I, *iodo-methane,* is most readily formed by the action of phosphorus and iodine upon methyl alcohol. The following quantities may be used: 35 parts CH_3OH, 100 parts I, and 10 parts red P. (for working details see *Ethyl iodide*).

Properties.—Methyl iodide is a colourless, mobile, refractive liquid, which turns brown on exposure to light from the liberation of iodine, b.p. 42·3°, sp. gr. 2·2529 at $\frac{25°}{25°}$. It has an ethereal odour, is difficultly combustible, and unites with water in the cold to form a hydrate, $2CH_3I.H_2O$.

Ethyl Iodide, $CH_3.CH_2I$, *iodo-ethane,* is formed by the action of hydriodic acid, or of phosphorus and iodine upon the alcohol, most readily by the latter method—

$$5C_2H_5OH + P + 5I = 5C_2H_5I + H_3PO_4 + H_2O$$

†*Process.*—Mix 10 grams of red phosphorus and 50 grams of *absolute* alcohol in a tubulated retort of 500 c.c. capacity, which is connected with a condenser and receiver. Next introduce little by little 100 grams of iodine, and allow the mixture to stand twenty-four hours. Then distil, and free the distillate from I by shaking with dilute NaOH; wash with water, dry over $CaCl_2$, and rectify by distillation. Both the P and the C_2H_5OH are in excess of the quantities calculated from the equation; the former hastens the reaction, while part of the alcohol forms ethyl phosphate.

Properties.—Ethyl iodide is a colourless refractive liquid, b.p. 72·4°, sp. gr. 1·9433 at $\frac{15°}{15°}$, which rapidly turns brown on exposure to light, owing to liberation of iodine, butane being also formed. It has a pleasant smell, is little soluble in water, readily in alcohol and ether, difficultly inflammable.

The bromides and iodides are chemically similar to methyl and ethyl chlorides, *e.g.* in their reactions with water.

Propyl Compounds.—These derivatives can exist in two forms according as the hydrogen atom displaced was attached to the end or central carbon atom of propane; *i.e.* they possess the general formulæ, $CH_3.CH_2.CH_2X$ or $CH_3.CHX.CH_3$. The first is the normal propyl derivative, the second the isopropyl compound. They can all be prepared by general methods, and are liquids insoluble in, and heavier than, water.

Isopropyl Iodide should be noted, as it is usually prepared from glycerin (which is a trihydric alcohol, p. 243) by distilling it with phosphorus and iodine, or with amorphous phosphorus and hydriodic acid in excess. The reaction is noteworthy as illustrating the manner in which hydriodic acid acts on the polyhydric alcohols, by replacing all the hydroxyl groups by hydrogen and iodine—

$$C_3H_5(OH)_3 + 5HI = \underset{\text{Iso-propyl iodide}}{CH_3.CHI.CH_3} + 3H_2O + 2I_2$$

It takes place in two stages—

$$\text{(i.)}\ C_3H_5(OH)_3 + 3HI = \underset{\text{Allyl iodide}}{C_3H_5I} + 3H_2O + I_2$$

$$\text{(ii.)}\ CH_2{:}CH.CH_2I + 2HI = CH_3.CHI.CH_3 + I_2$$

GROUP II.—DI-HALOGEN DERIVATIVES OF THE PARAFFINS.

Methylene Chloride, CH_2Cl_2, *di-chlor-methane*, *methene chloride*, can be prepared (1) by the action of chlorine on methyl chloride in sunlight; and (2) by the reduction of chloroform—

$$CHCl_3 + H_2 = CH_2Cl_2 + HCl$$

It is a colourless, oily liquid, with an odour like chloroform, b.p. 41·6°, sp. gr. 1·37 at 0°.

Di-chlor-ethanes, $C_2H_4Cl_2$, **Di-brom-ethanes,** $C_2H_4Br_2$, and **Di-iodo-ethanes,** $C_2H_4I_2$.—Of these there are two possible isomers, according as both the halogen atoms are attached to the same carbon atom, or one is attached to each of them.

Ethylene Chloride, $CH_2Cl.CH_2Cl$, *ethene chloride*, is the symmetrical form. This substance, originally known as *Dutch* *liquid*, is readily formed (1) by the direct union of ethylene and moist chlorine, by passing ethylene into a slightly heated mixture of 2 parts MnO_2, 3 parts NaCl, 5 parts H_2SO_4, and 4 parts H_2O; and (2) by the action of HCl or PCl_5 upon the di-hydric alcohol, glycol, $CH_2OH.CH_2OH$.

Properties.—Ethylene chloride is a colourless, thin oily liquid, b.p. 83·7° (cor.), sp. gr. 1·2808 at $\frac{0°}{4°}$. It has a sweetish odour and taste, is insoluble in water, soluble in alcohol and ether, and dissolves phosphorus. It burns with a green flame. It is said to be a useful anæsthetic in operations on the eye.

Ethylidene Chloride, $CH_3.CHCl_2$, *ethidene chloride*, the unsymmetrical derivative, is formed (1) by the direct action of chlorine upon ethyl chloride either in daylight or in presence of red-hot charcoal; (2) by heating aldehyde with PCl_5—

$$CH_3.CHO + PCl_5 = CH_3.CHCl_2 + POCl_3$$

but is best obtained (3) by fractional distillation of the by-products of chloral manufacture, in which it occurs along with ethylene chloride.

Properties.—Ethylidene chloride is a colourless liquid, b.p. 60·1°, sp. gr. 1·2039 at $\frac{0°}{4°}$. It resembles chloroform in taste and smell, and finds some employment as an anæsthetic. It is a very stable compound, being attacked only difficultly by KOH, and may be distilled unchanged over potassium.

Ethylene Bromide, $CH_2Br.CH_2Br$, *ethene bromide*, the symmetrical compound, can be obtained (1) by the action of bromine on ethyl bromide, but (2) is most readily and usually prepared by passing ethylene into bromine—

$$C_2H_4 + Br_2 = C_2H_4Br_2$$

†*Process.*—Pass ethylene (preparation, p. 53) through the wash-bottles (Fig. 31), which contain strong H_2SO_4 and NaOH respectively, by which it is freed from ether, CO_2 and SO_2. The second pair of Woulffe's bottles each contain 50 c.c. of bromine covered with water, and the gas is passed through till it is decolourised. The flask contains soda, which absorbs any bromine that escapes. When the reaction is finished, shake the product with NaOH, wash with water, dry over $CaCl_2$, and rectify by distillation. *The corks used in the bromine bottles must be well soaked in paraffin wax before use.*

Properties.—Ethylene bromide is a colourless oily liquid with a pleasant smell, b.p. 131·5° (cor.), sp. gr. 2·189 at $\frac{15^\circ}{15^\circ}$; it freezes to a crystalline mass, m.p. 9·2°. It is insoluble in water, but dissolves in alcohol and ether. On boiling with alcoholic potash, it forms vinyl bromide, C_2H_3Br, and acetylene; with aqueous potash, vinyl bromide; and with Na_2CO_3, glycol, $C_2H_4(OH)_2$.

Ethylidene Bromide, $CH_3.CHBr_2$, *ethidene bromide*, the unsymmetrical di-brom-ethane, is formed by brominating ethyl bromide in sunlight, and by the action of PCl_3Br_2 upon aldehyde in the cold. It is a liquid, b.p. 113°, sp. gr. 2·1029 at $\frac{15^\circ}{15^\circ}$.

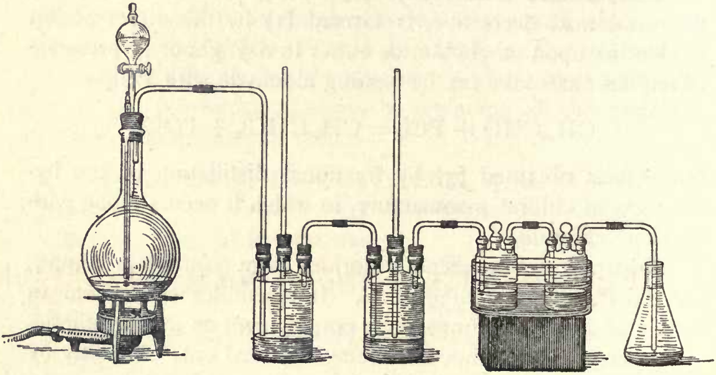


FIG. 31.

Ethylene Iodide, $CH_2I.CH_2I$, is formed by direct combination of iodine and ethylene by passing ethylene into a paste of iodine and alcohol. It forms colourless needles, m.p. 82°, which when heated in air are decomposed into C_2H_4 and I_2, but may be sublimed unchanged in an atmosphere of hydrogen or ethylene. It has an aromatic smell, and is insoluble in water, but soluble in ether and alcohol.

Ethylidene Iodide, $CH_3.CHI_2$, is formed by the action of AlI_3 or CaI_2 upon ethylidene chloride. This may be specially noted as an instance of iodine replacing chlorine. It is a liquid, b.p. about 178°, sp. gr. 2·84 at $\frac{0^\circ}{}$.

CONSTITUTION OF THE ETHYLENE AND ETHYLIDENE COMPOUNDS.

The constitution of these bodies has been so far assumed, but the reasons which lead to the formulæ assigned may now be discussed. With regard to ethylene chloride, it is natural to assume, from its mode of formation, that it is a symmetrical body, *i.e.* if it is granted that ethylene possesses the formula assigned to it, $H_2C{=}CH_2$ (see p. 55), we should expect it to form, when Cl_2 is added to it, the compound $ClH_2C{-}CH_2Cl$, and not $H_3C{-}CHCl_2$, since the former formula necessitates less internal alteration of the molecule.

But, apart from this reasoning, the fact that a chloride with other properties is actually produced by replacing the oxygen in acetaldehyde, $CH_3.CHO$, in which there is every evidence that the oxygen atom is only bound to one carbon atom, leads to the second formula, $CH_3.CHCl_2$, for ethylidene chloride; and as, according to our present knowledge, there are only two possible dichlor-ethanes, ethylene chloride must, by elimination of the last named, possess the formula $CH_2Cl.CH_2Cl$. A precisely similar argument, of course, applies to the bromo- and iodo- derivatives.

GROUP III.—TRI-HALOGEN DERIVATIVES.

Chloroform, $CHCl_3$, *trichlor-methane.*—This important substitution derivative of methane was discovered in 1831 by Liebig and by Soubeiran, by the first and second methods of formation. (1) By the action of alkalis upon tri-chlor-aldehyde (chloral, p. 131), sodium formate being also formed—

$$CCl_3.CHO + NaOH = CHCl_3 + H.CO_2Na$$

a process which is still employed when exceptionally pure chloroform is required. (2) It is formed when calcium hypochlorite acts upon dilute alcohol. The explanation of this reaction, which is employed on a large scale, is somewhat involved, but probably chloral is first formed, which is decomposed in turn by the alkali liberated from the bleaching powder, yielding chloroform (see Chloral, p. 131)—

$$8CaOCl_2 + 2C_2H_5OH = 2CHCl_3 + \underset{\text{Calcium formate}}{(HCO_2)Ca} + 5CaCl_2 + 2Ca(OH)_2 + 2H_2O$$

Manufacture.—The following is a sketch of its production by this method. A mixture of 3 parts 85 per cent. alcohol, diluted with 60 parts of water, is placed in an iron generating still provided with a stirrer and connected with a suitable condenser; 12 parts of bleaching powder, containing 35 per cent. available chlorine, are next added, and steam-heat is applied to raise the temperature to 40° (it must not rise above 60°). The distillate thus obtained consists of chloroform, water, and alcohol; it is collected and washed from alcohol, and afterwards rectified by a further distillation.

Chloroform can also be obtained (3) from methane or methyl chloride, by the action of chlorine in sunlight; and finally, (4) considerable quantities are now prepared by running acetone into a thin cream of bleaching powder and water—

$$2(CH_3)_2CO + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + \underset{\text{Calcium acetate}}{(CH_3.COO)_2Ca}$$

The proportions for this process, which gives an excellent yield, are 58 parts of acetone, and 166 parts of bleaching powder containing 35 per cent. available chlorine.

†*Process.*—Add 60 c.c. of acetone, little by little, with constant cooling, to a cream of 300 grams bleaching powder and 300 c.c. of water. Then distil off the chloroform by heating on a water-bath. The distillate consists of two layers, the lower of which is impure chloroform. Wash it once or twice with water, then dry over calcium chloride, and distil.

Purification.—For surgical purposes the chloroform obtained both from alcohol and acetone requires purification. It is first washed with water to remove traces of alcohol, then allowed to stand over strong H_2SO_4 (free from nitrous compounds) to char organic impurities, next freed from acid by Na_2CO_3 or lime-water, then dried over $CaCl_2$, and finally distilled at a temperature not exceeding 64°.

Properties.—Chloroform is a colourless liquid, b.p. 61·4°, sp. gr. 1·5 at $\frac{15^{\circ}}{15}$, and can be frozen to a solid, m.p. -70° It has a faint but characteristic smell and a sweet taste; is only slightly soluble in water, but mixes in all proportions with alcohol and ether. It burns, when mixed with alcohol and boiled, with a very smoky green-edged flame.

Chloroform is a powerful solvent, readily dissolving resins, fats, caoutchouc, alkaloids, sulphur, phosphorus, iodine, etc. It is antiseptic, and possesses a powerful anæsthetic action, which was discovered by Sir J. Simpson, of Edinburgh, in 1848, since which time it has been very largely used. In excess it is poisonous, hence care is needed in its administration. Warmed with alcoholic KOH, it yields potassium formate and chloride—

$$CHCl_3 + 4KOH = 3KCl + HCOOK + 2H_2O$$

Detection of Impurities.—Perfectly pure chloroform should not react either with litmus paper or $AgNO_3$ (absence of HCl and free Cl); neither strong H_2SO_4 nor KOH should turn it brown (absence of hydrocarbons and aldehyde). Alcohol is frequently present in small quantity, 1 per cent., to prevent the decomposition of the chloroform; its presence may be detected by the iodoform test (see p. 86).

Identification.—Chloroform undergoes many important reactions, which serve for its detection. Thus when a solution containing it is heated with alcoholic potash and *one* drop of aniline, the very disgusting odour of phenyl isocyanide is produced (the isonitrile test). This is a very delicate test; 1 part in 5000 can be detected by it. If chloroform is added to a solution of α- or β-napthol in KOH and warmed, an intense blue colour is obtained; addition of alcohol aids, water destroys it. An alcoholic solution of resorcinol, to which KOH and then chloroform is added, gives a beautiful red liquid on warming; dilution turns it violet. When chloroform is heated with Fehling's solution, it reduces it with precipitation of Cu_2O.

Bromoform, $CHBr_3$, *tri-brom-methane,* is found in crude bromine, and is formed (1) by decomposing bromal with alkalis, or (2) by acting with bromine and potash on alcohol or acetone. It is a liquid similar in appearance and smell to chloroform, b.p. 151°, sp. gr. 2·9045 at $\frac{15^\circ}{15^\circ}$, and freezes to a solid, m.p. 8°, but does *not* yield a formate on decomposition with KOH (distinction from $CHCl_3$).

Iodoform, CHI_3, *tri-iodo-methane,* is usually prepared by the action of iodine upon alcohol, although acetone and other substances may be used—

$$\underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + 4I_2 + 6KOH = CHI_3 + \underset{\text{Potassium formate}}{H.COOK} + 5KI + 5H_2O$$

†*Process.*—Mix 20 grams of alcohol with 40 grams of $Na_2CO_3.10H_2O$, and 200 grams of water, and heat in a flask to 60–80°, add gradually 20 grams of iodine, and filter off the iodoform which separates. Heat the filtrate to 80°, add 40 grams more soda, and pass in chlorine until no further separation of iodoform occurs. Collect the iodoform, wash thoroughly with water, and dry between filter paper. A new method now employed on a large scale depends upon the careful addition of a slight excess of dilute sodium hypochlorite to 50 parts KI, 6 parts acetone, and 2 parts NaOH, dissolved in 1–2 litres of water. The iodoform which separates is purified in the ordinary manner.

Properties.—Iodoform crystallises in characteristic six-sided, yellow tables, sp. gr. 2, which smell like saffron. It melts at 119°, and sublimes on heating, with partial decomposition, iodine and HI being formed; it is, however, volatile in a current of steam. It is insoluble in water, but soluble in ether, alcohol, and carbon disulphide. Its solution in alcohol or CS_2 (especially CS_2) is very sensitive to light; iodine is liberated, and methylene iodide produced. Boiling aqueous KOH decomposes iodoform with formation of potassium formate, alcoholic KOH forms methylene iodide. If mixed with finely divided moist silver acetylene is evolved.

It is an anæsthetic, with special action on the muscles.

Identification.—A solution of phenol and solid KOH, gently warmed with an alcoholic solution of iodoform, gives a red substance soluble in alcohol with a carmine red colour. Its reactions with napthol and resorcinol are similar to those of chloroform (p. 75).

GROUP IV.—TETRA-HALOGEN DERIVATIVES.

Carbon tetra-chloride, CCl_4, *tetra-chlor-methane*, is formed (1) by the action of chlorine on methane in sunlight; but most readily (2) by passing chlorine into boiling chloroform containing a little iodine in solution; or (3) by passing chlorine and carbon bisulphide vapours through a red-hot tube, decomposing the sulphur chloride formed simultaneously by potash, and rectifying. It is a thin colourless liquid, with aromatic smell, b.p. 76·7°, sp. gr. 1·63 at $\frac{0^\circ}{4^\circ}$. It is insoluble in water, soluble in alcohol and ether; it is decomposed by alcoholic KOH, thus: $CCl_4 + 4KOH = CO_2 + 2H_2O + 4KCl$ (compare chloroform).

Carbon tetra-bromide, CBr_4, *tetra-bromo-methane*, occurs in crude bromine, and can be prepared by acting on $CHBr_3$, CHI_3, or CS_2, with bromine in presence of iodine. It is a white crystalline solid, m.p. 91°, b.p. 189·5°, sp. gr. 3·42, has a camphor-like smell, and very readily sublimes.

Carbon tetra-iodide, CI_4, *tetra-iodo-methane*, is obtained by heating CCl_4 with AlI_3 or CaI_2. It is a red solid, crystallises in octahedra, sp. gr. 4·32 at $\frac{20^\circ}{\cdot}$, and slowly decomposes in air.

GENERAL REMARKS ON THE HALOGEN DERIVATIVES.

Two general methods of production have been already mentioned on pp. 64, 65. It may be noted that they are also notably formed (1) by addition of halogen hydrides to olefines; (2) by addition of a molecule of a halogen to an olefine; and (3) sometimes by the action of PCl_5 on bodies containing a CO group, *e.g.* $CH_3.CHO$.

Properties.—The haloid derivatives of the paraffins are very little soluble in water, but dissolve readily in all proportions in alcohol and ether, and also in acetic acid. The liquids are generally colourless and possess an ethereal smell, and are stable with the exception of the iodine compounds, which redden when exposed to light, owing to the liberation of iodine.

The chlorine derivatives boil at a lower temperature than the bromine compounds, and those than the iodine derivatives, and the primary derivatives possess a higher boiling point than the secondary. They burn with a green-edged flame, and their inflammability decreases with increase of the amount of halogen.

It is important to remember that $AgNO_3$ cannot be employed as a reagent for the detection of the halogens, although under certain circumstances the halogen derivatives do react with it. The halogens can be displaced by moist silver oxide with introduction of hydroxyl (see Alcohols). Many of the haloid paraffins also yield alcohols when treated under pressure with water or a dilute solution of KOH; but, on the other hand, alcoholic potash splits off a molecule of the halogen hydride and forms olefines (see p. 56).

Nascent hydrogen from sodium amalgam and dilute alcohol, and from Zn and HCl, reduces the halogen compound to the corresponding hydrocarbon, *e.g.*—

$$CHCl_3 + 3H_2 = CH_4 + 3HCl$$

Ammonia acts on the monohaloid derivatives, forming amines (p. 163).

CHAPTER XII.

ALCOHOLS.

THE general term "alcohol" is given to a class of bodies composed of carbon, hydrogen, and oxygen, which are derived from hydrocarbons by the replacement of one or more atoms of hydrogen by an equal number of hydroxyl (OH') groups; thus from ethane are derived ethyl alcohol, C_2H_5OH, and glycol, $C_2H_4(OH)_2$. They are termed mono-, di-, or polyhydric alcohols, according to the number of OH groups which they contain.

The name was originally applied solely to spirits of wine, and is supposed to be a corruption of the term *vinum alcalisatum* to *vinum alcoholisatum*, whence alcohol vini.

The alcohols are substances which bear a certain resemblance to the metallic hydroxides. Thus the OH is replaceable by acid radicles; for example, just as KOH yields KCl, $KHSO_4$, $KC_2H_3O_2$, so methyl alcohol, CH_3OH, yields CH_3Cl, CH_3HSO_4, and $CH_3C_2H_3O_2$.

The number of hydrogen atoms replaceable by hydroxyl in a hydrocarbon is, however, practically limited by the number of carbon atoms in the molecule, since, except under special circumstances, compounds containing more than *one* hydroxyl group to each atom of carbon cannot be obtained; *e.g.* glycerin,

$C_3H_5(OH)_3$, the first stable alcohol which contains three hydroxyl groups, also contains three carbon atoms.

Isomerism of Alcohols.—The two first paraffins, methane and ethane, each yield only one mono-hydric alcohol; propane, butane, and the higher paraffins can yield isomeric forms, the isomerism of which is due to two different causes: (i.) that produced by the *position in the hydrocarbon* of the replaced hydrogen atom; and (ii.) that owing to the isomerism of the hydrocarbon itself.

Thus in methane and ethane the hydrogen atoms are presumably of the same relative value, and only one alcohol is obtainable in each case, viz. $H.CH_2OH$, and $CH_3.CH_2OH$; but propane, $CH_3.\overset{(a)}{CH_2}.\overset{(b)}{CH_3}$, can yield two alcohols, viz. (i.) $CH_3.CH_2.CH_2OH$ and (ii.) $CH_3.CH(OH).CH_3$, according as the OH group is attached to the carbon atom (*b*) or (*a*), because the carbon atoms (*a*) and (*b*) occupy relatively different positions in the molecule. Similarly, the two butanes, $CH_3.CH_2.CH_2.CH_3$ and $(CH_3)_2CH.CH_3$ can *each* yield two isomers according to the carbon atom to which the OH is linked. Thus the first yields (i.) $CH_3.CH_2.CH_2.CH_2OH$ and (ii.) $CH_3.CH_2.CH(OH).CH_3$; and the second (iii.) $(CH_3)_2CH.CH_2OH$ and (iv.) $(CH_3)_3COH$.

It will be seen that the alcohols derived from methane and ethane, one of those from propane (i.), and two of those from butane (i. and iii.) contain the group $—CH_2OH$, which is characteristic of **primary alcohols.** The second one derived from propane and the second from butane contain the divalent group $=CHOH$, that is distinctive of **secondary alcohols**; while the fourth alcohol derived from butane contains the trivalent group $\equiv COH$, and is a **tertiary alcohol.**

All alcohols (from whatever hydrocarbon they are derived) comprise one or other of the above-named groups; so that there may be normal-primary, and iso-primary alcohols derived from isomeric hydrocarbons. Thus the alcohols yielded by the butanes may be named (i.) normal primary butyl alcohol; (ii.) secondary butyl alcohol; (iii.) iso-primary butyl alcohol; and (iv.) tertiary butyl alcohol, respectively.

Nomenclature of Alcohols.—Kolbe proposed that, for the sake of simplicity, the simplest alcohol, CH_3OH or $H.CH_2OH$, should be called **carbinol**, and that all others should be looked upon as derived from it, and designated accordingly; thus ethyl alcohol would become methyl carbinol, the propyl alcohols would be termed ethyl and di-methyl carbinol respectively, and so forth. This proposal has not, however, received universal acceptance, and the alcohols are more generally named according to the hydrocarbon radicles which they contain, the word "alcohol" being employed as the generic termination.

MONOHYDRIC ALCOHOLS OF THE $C_nH_{2n+1}OH$ SERIES.

Methyl alcohol,	CH_3OH	Butyl alcohols,	C_4H_9OH
Ethyl alcohol,	C_2H_3OH	Pentyl alcohols,	$C_5H_{11}OH$
Propyl alcohols,	C_3H_7OH	Hexyl alcohols,	$C_6H_{13}OH$, etc.

The alcohols derived from the hydrocarbons of the methane series by replacing *one* hydrogen atom by hydroxyl, *i.e.* the saturated monohydric alcohols, must naturally receive earliest consideration, and of these that derived from methane is the simplest.

Methyl Alcohol, CH_3OH or $H.CH_2OH$, *methyl hydrate, carbinol, wood spirit, wood naphtha.*

(1) The chief source of methyl alcohol is the watery distillate obtained in the destructive distillation of wood; indeed, it was in that substance that Boyle first discovered it.

Manufacture.—The above-mentioned liquid, which contains besides the alcohol, acetone, acetic acid, and other substances, is separated by settling and filtration from suspended tarry matters, and then distilled in copper stills heated by steam. The first tenth of the distillate is then distilled off caustic lime, again distilled after the addition of a little sulphuric acid, and finally rectified over quicklime. Each ton of wood distilled yields from 1 to 3 gallons of wood spirit.

(2) Considerable quantities of the alcohol are also obtained from the spent wash or "vinasse" left when alcohol is prepared from beet-root molasses.

Manufacture.—The "vinasse" is evaporated to dryness, the residue calcined, and the vapours condensed. The liquid so obtained contains tri-methylamine, ammoniacal salts, methyl cyanide, and methyl alcohol. It is neutralised with H_2SO_4, and again distilled. The distillate contains the cyanide and the alcohol, and is freed from the former by distillation over lime. The weak alcohol which is so obtained is concentrated by means of quicklime.

Ordinary wood spirit varies very much in strength, the amount of alcohol in it varying from 45 to 95 per cent.

Preparation of the Pure Alcohol.—In order to prepare the pure alcohol, the acetone present in crude wood spirit may be partially removed by fractional distillation; or the crude spirit is saturated with calcium chloride, the acetone distilled off, and the alcohol separated from the calcium chloride by adding water and then distilling. The still impure methyl alcohol thus obtained is dehydrated by lime, heated to the boiling point, anhydrous oxalic acid dissolved in it, and then allowed to cool. Crystals of di-methyl oxalate separate out, and are washed with water till the washings no longer give the iodoform reaction (see p. 86) showing the absence of acetone; they are then boiled with water or dilute soda, and the alcohol distilled off. It may then be dehydrated by means of lime or baryta.

(3) Almost pure alcohol may be obtained by saponifying oil of winter-green with potash and distilling off the alcohol. And (4) it is also formed synthetically by heating methyl chloride with KOH for some days to 100°—

$$CH_3Cl + KOH = CH_3OH + KCl$$

or (5) by heating it to 200° with potassium acetate and acetic acid, and saponifying the product with KOH.

$$\text{(i.)}\quad CH_3Cl + HC_2H_3O_2 = CH_3C_2H_3O_2 + HCl$$
$$\text{(ii.)}\quad CH_3C_2H_3O_2 + KOH = CH_3OH + KC_2H_3O_2$$

Properties.—Pure methyl alcohol is a colourless, limpid liquid, b.p. 65·8–66° (cor.), sp. gr. $\frac{15^\circ}{15^\circ}$, 0·7972. It has a pure spirituous odour, and burns with a pale blue flame. It mixes with water in all proportions, heat being evolved and contraction taking place, this latter being greatest when the proportions present are 1 mol. CH_4O : 3 mols. H_2O. It mixes with water, alcohol, and ether, and possesses great solvent powers, dissolving oils, fats, resins, etc., with ease, and hence is much used as a solvent. Anhydrous copper sulphate is slightly soluble in it, although the hydrated salt is not. It combines with many salts to form combinations in which it acts as "alcohol of crystallisation," *e.g.* $CaCl_2.4CH_3OH$, $LiCl.3CH_3OH$, and $CuSO_4.2CH_3OH$; the first of these is employed in purifying it.

On oxidation it yields formic aldehyde and formic acid, the latter being also formed when it is heated with soda-lime. When taken internally it acts as an intoxicant.

Methyl alcohol finds considerable employment in the manufacture of aniline colours, for which purpose it should be free from ethyl alcohol and acetone; it is also employed for making varnishes and as a source of heat.

Identification.—The following tests assist in the detection of methyl alcohol: It gives, when heated with H_2SO_4 and sodium salicylate, the odour of oil of winter-green. When it is oxidised by $K_2Cr_2O_7$ and H_2SO_4 it yields formic acid, which can be distilled off, and gives a black precipitate or silver mirror with $AgNO_3$ solution. It gives no iodoform when warmed with KOH and iodine (*difference from ethyl alcohol*).

Constitution.—Some of the reactions of methyl alcohol are specially interesting, because they help to elucidate its constitution, and are also typical of those undergone by the higher members of the series. It has been already pointed out (p. 78) that the monohydric alcohols bear some resemblance to metallic hydroxides, *i.e.* they may be looked upon as hydroxides of organic radicles.

Thus methyl alcohol is a neutral substance, and yet it possesses slight basic properties, for its hydroxyl can be replaced by halogens similarly to that, for example, of KOH. Thus—

$$KOH + HCl = KCl + H_2O$$
$$CH_3OH + HCl = CH_3Cl + H_2O$$

The latter reaction is realisable, though not readily, with the acid itself; but if PCl_5, PCl_3, or $POCl_3$ are employed, it is quite easy to prepare methyl chloride (compare p. 65); *e.g.*—

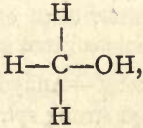
$$CH_3OH + PCl_5 = CH_3Cl + POCl_3 + HCl$$

and similar reactions occur with the other halogen acids and compounds of phosphorus, although in the last cases it is preferable to employ the elements P and Br, or P and I to produce CH_3Br and CH_3I respectively (see p. 66).

Methyl alcohol reacts also with other acids to form "ethereal salts," or "esters," in a quite analogous fashion to those produced by KOH. Thus—

$$\begin{gathered} KOH + HNO_3 = KNO_3 + H_2O \\ CH_3OH + HNO_3 = CH_3NO_3 + H_2O \\ KOH + H_2SO_4 = KHSO_4 + H_2O \\ CH_3OH + H_2SO_4 = CH_3HSO_4 + H_2O \end{gathered}$$

Methyl alcohol also dissolves potassium and sodium with the formation of the corresponding methoxides or methylates CH_3OK and CH_3ONa, which can be obtained from their solution in the alcohol as white solids, which are deliquescent, alkaline, and absorb CO_2. These substances are thus analogous to the corresponding hydroxides.

It will be recognised that these reactions with acids and metals lead inevitably to the conclusion that methyl alcohol contains the group OH, or that its formula is correctly represented as  $\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}OH}$, which is methane having a hydrogen atom replaced by hydroxyl.

The second member of the Alcohol series is—

Ethyl Alcohol, $CH_3.CH_2OH$, *spirits of wine, methyl carbinol.* Amongst the very oldest manufactures of the world must be placed that of producing the various fermented liquors which serve as more or less intoxicating beverages for various nations, and the existence in these of a substance to which ultimately the term "alcohol" was given, was proved by the result of investigations in the art of distillation.

It is by this same means, *i.e.* by fermentation of various saccharine solutions and distillation of the resultant product, that alcohol is prepared to-day. The manufacture of strong alcohol is described on p. 88; and a typical reaction is that which occurs when grape sugar undergoes fermentation—

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

This equation represents the principal reaction, which accounts for 95 per cent. of the sugar; the remaining 5 per cent. goes to form other substances, among which are glycerin and succinic acid.

Experiment 13.—The validity of the above equation may be qualitatively shown thus: Fit a large flask with a perforated cork and tube, as in *a*, Fig. 32; introduce into it a solution of 40 grams of glucose in 1½–2 litres water, add a little yeast, cork the flask, and insert the tube into a bottle (*b*) containing clear lime-water. Keep the solution in the flask just warm (20°); it will ferment readily, and the formation of CO_2 will be shown by the production of $CaCO_3$ in the lime-water. When the fermentation is over, connect the flask by means of a bent tube with a condenser, distil off about 100 c.c., and test for alcohol in it by the reactions given on p. 86.

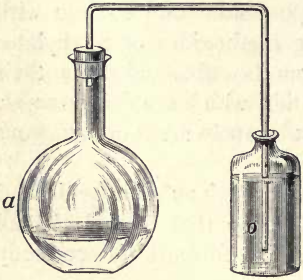


FIG. 32.

Preparation of Absolute Alcohol.—Anhydrous alcohol is obtained from the above-mentioned strong spirit. This always contains some water, from which it is freed by the use of absorbents, such as freshly ignited K_2CO_3, $CaCl_2$, CaO, or BaO. Of these lime is generally used.

†*Process.*—Place quicklime in a flask or other vessel and add sufficient alcohol to cover it, allow to stand for some hours at 40° and afterwards distil, rejecting the first and last portions. Repeat this process if the alcohol contained more than 5 per cent. of water.

The last traces of moisture are removed either by carefully adding a small quantity of sodium to the alcohol and again distilling; or, better, by adding to the lime during the last treatment a small quantity of fresh baryta, which, when the alcohol is anhydrous, dissolves in it with the formation of a yellow liquid, which on distillation yields absolute alcohol. Commercial absolute alcohol usually contains about 0·5 per cent. of water, from which it may be freed as described.

Alcohol may be synthetically produced (*1) by dissolving ethylene in H_2SO_4, diluting the ethyl hydrogen sulphate formed (p. 55) with water, and then distilling it—

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4$$

This is an important method, because by its means the synthesis of alcohol from inorganic materials can be accomplished; for carbon and hydrogen unite under the influence of the electric discharge to form C_2H_2, this in its turn unites with nascent hydrogen to form C_2H_4, and the reactions given complete the synthesis. It may also be formed (2) from ethyl bromide or iodide by the action of moist Ag_2O (which acts as AgOH), or from ethyl chloride by heating under pressure with dilute alkalis.

$$C_2H_5Cl + KOH = C_2H_5OH + KCl$$

Properties.—Pure ethyl alcohol is a transparent, colourless, mobile liquid, b.p. 78·2–78·5°; it solidifies at $-130·5°$, and its sp. gr. is 0·795 at $\frac{15°}{15°}$. It has a pleasant ethereal odour and a burning taste; is inflammable, burning with a pale blue flame; and its vapour mixed with the proper quantity of air forms an explosive mixture. It is very hygroscopic, and mixes with water in all proportions with contraction of volume and evolution of heat; the contraction is greatest when the proportions employed are $C_2H_6O : 3H_2O$. If, however, 2 parts of alcohol are mixed with 1 part of snow, a freezing mixture is produced. In a concentrated condition it acts as an inflammatory poison, and when dilute produces intoxication.

It is a most useful solvent for many organic bodies, such as fats, resins, and alkaloids, and it dissolves many gases and inorganic salts. In the latter case some curious instances occur; thus it dissolves LiCl, but neither KCl nor NaCl; $CaCl_2$, $SrCl_2$, and $Ca(NO_3)_2$ are soluble, but neither $BaCl_2$, $Sr(NO_3)_2$, nor $Ba(NO_3)_2$. It also combines with many salts, forming compounds in which it plays the same part as water of crystallisation.

Alcohol coagulates albumen, so preventing putrefaction. Oxidising agents, according to their strength, form aldehyde and acetic acid. Chlorine attacks it violently, and forms chloral alcoholate. Heated with strong sulphuric acid, it yields, according to circumstances, ether or ethylene. Like methyl alcohol it reacts with metals, forming ethoxides or ethylates, and it also forms salts in a similar fashion.

Absolute alcohol gives no blue colour to anhydrous copper sulphate, produces no turbidity with benzene, and does not give a precipitate of $Ba(HO)_2$ if BaO dissolved in absolute alcohol is added to it. It also gives a green colouration with sodium amalgam and anthraquinone, but if water is present a red colour is formed.

Identification.—Alcohol may be detected in an aqueous solution by adding to it a little NaOH or KOH and a slight excess of iodine; on gently warming, six-sided star-shaped crystals of iodoform will be produced. This reaction (*Lieben's*) is so delicate that $\frac{1}{2000}$ part of alcohol may be recognised. It must be remembered, however, that many other substances form the same compound, *although methyl alcohol does not yield it.* When alcohol is acted upon by acetyl chloride (p. 158), or heated with a little sodium acetate and conc. H_2SO_4, the fragrant odour of ethyl acetate is developed. Or the liquid containing alcohol may be distilled, the distillate rectified till anhydrous, and a determination of its boiling point made. If the alcoholic liquid is boiled with a little $K_2Cr_2O_7$ solution and dilute H_2SO_4, the smell of aldehyde is obtained; and if the mixture is then distilled, and the distillate warmed with KOH, a yellowish brown colour indicates the presence of alcohol.

Constitution.—The formula of alcohol follows from similar considerations to those adduced for that of methyl alcohol, to which substance it bears a strong chemical resemblance. It is also supported by its formation from ethyl chloride, which can be prepared direct from ethane.

FERMENTATION. MANUFACTURE OF ALCOHOL.

The formation of alcohol by a fermentative process is important as affording the first instance of the production of organic compounds (if marsh gas is excepted) by means of living organisms. It is necessary, therefore, to say a few words on the subject of fermentation.

Fermentation.—Many organic substances, when exposed to the air, undergo a rapid decomposition, very frequently without any apparent cause. These decompositions have been proved to result from the action either of living organisms (*bacteria* or *fungi*) or of chemical ferments known as *enzymes*, which are the product of vital action, although themselves unorganised. The organisms need in most cases the presence of air and also of nitrogenous matter, in order to grow and produce the changes noted. All ferments are destroyed or rendered inactive by high temperatures, at least under ordinary conditions.

How the organisms act is not accurately known. It is thought by some that they themselves actually produce the transformations by their life-processes; others think that they secrete an enzyme, which in its turn effects the change. As an example in support of the latter theory may be cited yeast, which secretes the ferment *invertase* that possesses the property of transforming cane sugar into dextrose and levulose.

Fermentation products may be neutral, acid, or basic, and it may be noted that the bacteria and moulds form more simple products than do the known enzymes.

Alcoholic fermentation is brought about by many different organisms, the principal of which is the ordinary yeast-plant, *Torvula* or *Saccharomyces cerevisiæ*, the ferment that is made use of by brewers and distillers for fermenting the various worts with which they are severally concerned.

When viewed microscopically, it is a round or oval, somewhat globular object (Fig. 33), and grows, when in a suitable medium, by budding or gemmation. These buds often adhere to the parent and themselves undergo subdivision, with the result that sometimes a string of them is formed which might be mistaken for other organisms.

Manufacture of Alcohol.—The first stage in the manufacture of alcohol is the preparation of the *wort*, a saccharine solution of not more than 1·04 sp. gr. Many kinds of grain, potatoes, etc., may be used in its production, but mixtures of malt, rye, barley, oats, maize, and rice are chiefly employed in the United Kingdom.

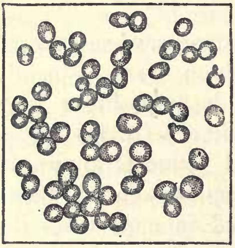


FIG. 33.

By the term *malt* is usually meant barley, which has been first steeped in water till soft, then piled in heaps and allowed to germinate, and finally kiln-dried to destroy the vitality of the seed.

In any case a certain proportion of malt is necessary, because, as a result of the processes just described, it contains a soluble ferment called *diastase*, which possesses the power of transforming the starch present in the grain into a fermentable sugar. A mixture of two or more kinds of grain has been shown to give a larger yield of alcohol than one kind only.

In preparing the wort, about one part of malted barley and two or three parts of ordinary grain (the grist) are taken and crushed up into a tolerably fine condition. This mixture is then extracted ("mashed") once or twice with warm water at 60°–65°, and the infusion allowed to stand for some hours, during which time the diastase converts the starch into dextrin and malt sugar (maltose).

After that the cool wort is mixed at a temperature of about 23° with yeast, and the fermentation of the wort proceeds during four or five days, at the end of which time its specific gravity will be reduced to about 1·0, and it will be ready for distillation.

By suitable distillation a spirit containing 90 per cent. by weight of alcohol can be readily obtained, from which absolute alcohol can be prepared as already described. If the ordinary form of still is employed, it requires repeated fractionation to separate the alcohol from the accompanying water; consequently many attempts have been made to separate the two liquids by a continuous operation, and many stills embodying the same principles as Wurtz's fractionating bulbs (see p. 7) have been devised. The one commonly used in England is known as Coffey's still, and is figured in diagrammatic form in Fig. 34.

It consists of two columns, E and G, known respectively as the "analyser" and "rectifier;" and, after heating them by steam, omitting minor details, it is employed as follows:—

The fermented wort, or *wash* as it is technically termed, is pumped up from the reservoir by the pipe B, and passes down the rectifier by the pipe CC, which forms a series of zigzags between

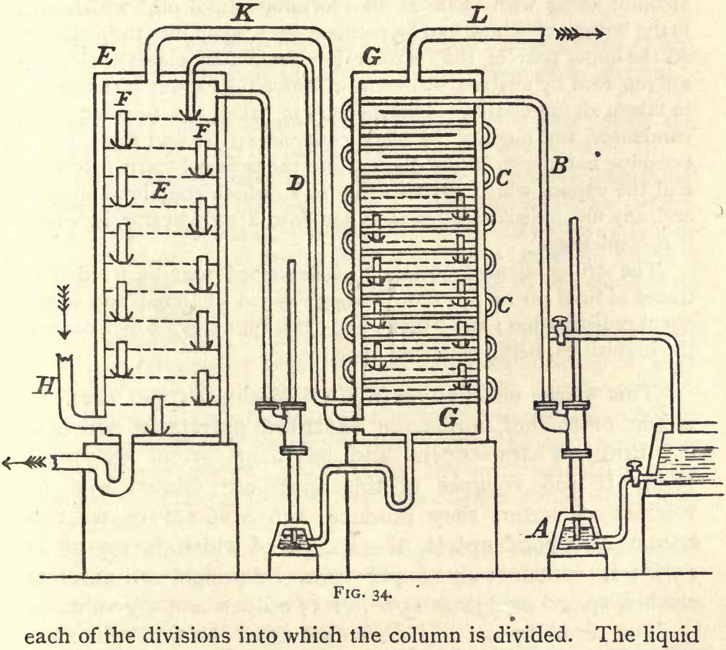


FIG. 34.

each of the divisions into which the column is divided. The liquid is then discharged into the analyser E, where it meets ascending vapours, the pressure of which prevents it falling down through the perforations of the plates, and it therefore descends by the tubes F F, which discharge the overflow of liquid from one diaphragm on to that next below it. As it descends through these plates it is met by a current of steam coming in through the pipe H, which causes it to boil and volatilises the alcohol. It is thus, by the time it reaches the bottom of the column, deprived of its alcohol, and passes away as spent wash. It will be readily seen that as the steam and alcoholic vapour ascend through the perforated plates they are washed by the short columns of liquid on them, which condense large portions of the aqueous vapour, while the alcohol passes out by the pipe K into the rectifier. In the rectifier it again passes up through a series of perforated plates, where by condensation there are quickly formed layers of liquid as in the analyser, but the cooling and washing effect is intensified by the presence of the pipes C C, which contain the cool wash. More water-vapour is condensed there along with the *feints*, which consist of higher-boiling alcohols along with some alcohol forming "fusel oil," which falls to the bottom of G, and can be pumped back again into the analyser. At the upper part of the rectifier the perforated plates cease, and are replaced by shelves, by means of which the vapour is compelled to take a zigzag course. This portion is called the finished-spirit condenser, and most of the spirit condenses here and flows, by an exit-pipe not shown in the diagram, to the finished-spirit reservoir, and the vapour which passes away at L, which contains aldehyde and any uncondensed alcohol, is led into a refrigerator, in which it is condensed.

The strong alcohol obtained as described may be freed from traces of fusel oil by filtration through wood charcoal and subsequent redistillation ; the "first" and "last runnings," which contain the impurities, being collected apart.

This spirit, on dilution till it contains 84 per cent. by weight of alcohol, forms the **rectified spirits of wine** of the British Pharmacopeia, and has a sp. gr. of 0·8382 at $\frac{15{\cdot}6^\circ}{15{\cdot}6^\circ}$. If 100 volumes of this spirit are diluted with 60 volumes of water, they produce 156 volumes of what is known as **proof spirit,** the sp. gr. of which is 0·9198 at 15·6° ; it contains 49·24 per cent. by weight of absolute alcohol, sp. gr. 0·7938 at 15·6°, or 57·06 per cent. by volume.

The term "proof" is a survival from the time when the strength of spirit was roughly tested by moistening gunpowder with it and then igniting it. The weakest spirit which would ignite the gunpowder when the alcohol was burnt off was "proof spirit ;" while above and below that strength it was termed "over" and "under" proof respectively.

Methylated Spirit.—In consequence of the high duty upon rectified spirit, it is much too costly to use as a solvent for manufacturing purposes, *e.g.* in making varnishes, polishes, etc. For this purpose, therefore, the Board of Inland Revenue permit the use of a mixture of 1 part wood spirit and 9 parts rectified spirit to be sold under the above name. Latterly, to make it still less drinkable and more difficult to purify, $\frac{3}{8}$ per cent. of mineral naphtha, 0·8 sp. gr., has been added. This latter addition, however, renders it useless for many laboratory purposes.

ALCOHOLIC BEVERAGES.

Under this heading may be considered various intoxicating liquors which owe their properties to the presence of alcohol.

Beer is a liquor of ancient origin, and is a product of the fermentation by yeast of malted grain, usually barley.

In the manufacture of beer, the malt, after preliminary crushing, is run along with water at 70–75° C. into the *mash-tun*, where, when thoroughly mixed, the whole mixture should possess a temperature of 60–65° C., at which heat it is allowed to stand for $1\frac{1}{2}$–2 hours to allow of the diastatic transformation of the starch into maltose and dextrin (see p. 276).

The *mash liquor*, or *sweet wort*, is boiled in the *wort boiler* for 1–$1\frac{1}{2}$ hour, after being mixed with the necessary quantity of hops. The hops serve the double purpose of imparting a bitter aromatic taste to the finished product, and also, owing to the tannin matter which they contain, of helping to clear the beer by the precipitation of albuminous matter: while boiling the wort coagulates these albuminous matters, and also destroys disease germs which may be present.

From the boiler the wort is run into the *hop-back*, a large vessel in which it is strained from the hops as it is run to the *coolers*, and from them over the refrigerators to the *fermenting tuns*, where it should possess a temperature of 15° C.

In the fermenting tuns the wort is mixed with the necessary amount of yeast, the fermentation begins at once, and the temperature will perhaps become 21° C. in about 60 hours; it is not allowed to rise above this. It is allowed to proceed till the desired amount of *attenuation* (loss of specific gravity) is attained when the yeast is separated from the beer in various ways. The beer is then racked into casks for immediate use or for storage. A slight fermentation continues in the cask, which makes the beer stronger and less sweet, and charges it with carbonic acid gas.

The strength of the beer produced varies according to the purpose for which it is required.

Porter or **Stout** is manufactured similarly, the dark colour being due to the introduction of half-burnt or caramelised malt.

Wines are liquors prepared by allowing the expressed juice of the grape, known as *must*, to undergo spontaneous fermentation owing to the germs present on the fruit itself. The grapes are crushed by various methods, and, if white wines are required, are separated from the residual skins, stalks, etc. (*the marc*), as soon as possible. The wines produced from such "must" owe their colour to the oxidation of the extractive matter of the juice. In the case of coloured wines, the marc is not separated from the must until *after* fermentation, when, owing to the joint action upon the alcohol and acid then produced, a certain amount of the colouring matter (ænolin) is extracted.

The grape juice is fermented in large barrels at 10–12° C. for 12–14 days. At the end of this time the clear "young" wine is drawn off the lees, first into vessels, where it is allowed to rest, and then racked into casks, where it matures. During this last stage a second slow fermentation occurs, and as the amount of alcohol slowly increases there is deposited a crust of potassium hydrogen tartrate and calcium tartrate along with albuminous and colouring matters, which is known as *argol*. This acid salt of potassium is present along with several other acids in the original juice, and differs from them in being much less soluble in dilute alcohol than in water, hence its precipitation.

During the maturing of the wine, either in casks or bottle, the special flavour or "bouquet" is developed; this is due to the formation of various ethereal salts, which are formed from the alcohol or alcohols present. This bouquet differs with different wines, and has been shown to be owing, at least in part, to the yeasts characteristic of the various districts.

Spirits.—*Brandy*, properly so called, is made from the spirit distilled from certain white French wines. After dilution this is stored in vats, and allowed to mature. If stored in oak vats it becomes yellow and yields pale brandy; if coloured with caramel it forms brown brandy. As imported into this country it contains about 50 per cent. by weight of alcohol, or is 1–2 over proof.

Rum is spirit obtained from molasses, and owes its flavour to ethyl butyrate. It is generally imported at 20 over proof.

Whiskey is largely made from malt only, sometimes from malt and rye. Scotch whiskey is generally bonded at 11 over proof, and Irish whiskey at 25 over proof.

Brandy, rum, and whiskey cannot be sold of less strength than 25 under proof.

Gin, or Geneva (from the French *genièvre*, "the juniper"), is a grain spirit mainly made from malt and rye, and specially flavoured with various aromatic substances, such as angelica root, cardamons, juniper, liquorice powder, etc. Hollands, the Dutch spirit, is flavoured by juniper. Absinth is a form largely used in France, and flavoured with wormwood. It is generally sold by the rectifiers about 17–22 under proof. Its lowest limit of sale is 35 under proof.

The following are *approximately* the percentage amounts by weight of alcohol in some alcoholic liquors :—

Lager beer	4 per cent.	Madeira ...	16 per cent.
Burton ale ...	6 ,,	Port ...	18 ,,
London porter	6 ,,	Brandy ...	50 ,,
Claret ...	8 ,,	Whiskey ...	60 ,,
Sherry ...	15 ,,		

ALCOHOLOMETRY.

By the term "alcoholometry" is meant the art of estimating the amount of alcohol in a spirituous liquid, whatever be the method employed.

The chief processes which are now used to determine the strength of an alcoholic liquid, depend upon ascertaining either the specific gravity of the liquid itself, or, since alcoholic liquors frequently hold other substances in solution, that of the liquid obtained by distilling off half to three-quarters of a given volume of the liquor, and making the distillate up to the original volume with distilled water. If alcohol and water underwent no contraction when mixed, it would then be easy (knowing the specific gravity of alcohol itself) to calculate, by means of the well-known formula, the percentage of alcohol present in the mixture. Alcohol and water do, however, undergo contraction of volume when mixed, and it has therefore been necessary to ascertain directly the specific gravity of the two liquids when mixed together in all proportions and at different temperatures. This has been done with great accuracy by Gilpin, Tralles, Gay Lussac, Fownes, and others; so that, if the specific gravity of dilute alcohol is carefully ascertained, on reference to their tables the percentage amount present can be at once ascertained.

For excise purposes the specific gravity is determined by Sikes' hydrometer, shown in Fig. 35, which is made of hard metal and gilded. The stem is graduated from 0 at the upper to 10 at the lower end, with intermediate graduations for every $\frac{2}{10}$ of a division. It is also provided with nine other weights (numbered respectively 10 to 90), which, by means of a slit in them, can be fixed on the stem; these increase the range of the instrument.

Since in England the standard of strength is not absolute but proof spirit, this hydrometer is graduated accordingly, and can only be used in conjunction with tables.

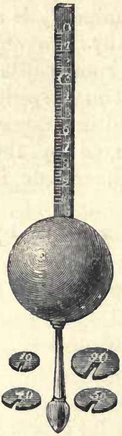


FIG. 35.

CHAPTER XIII.

ALCOHOLS—Continued.

GENERAL REMARKS ON THE MONOHYDRIC ALCOHOLS.

OF the following general methods of formation, the first three have already received some illustration during the study of methyl and ethyl alcohols.

1. Alcohols can be prepared from mono-haloid hydrocarbons by the action upon them of KOH, freshly precipitated moist Ag_2O, PbO, and even occasionally of water alone. KOH is of little service, but moist Ag_2O, which acts as if it were AgOH, is very useful—

$$C_2H_5I + AgOH = C_2H_5OH + AgI$$

2. A method which is frequently of great use consists in first transforming the haloid derivative into an ethereal salt (see p. 107) of acetic acid, either by heating with silver acetate, or with a mixture of potassium acetate and glacial acetic acid, and then saponifying the resulting salt with KOH—

$$\underset{\text{Propyl chloride}}{CH_3.CH_2.CH_2Cl} + AgC_2H_3O_2 = \underset{\text{Propyl acetate}}{CH_3.CH_2.CH_2(C_2H_3O_2)} + KCl$$

$$CH_3.CH_2.CH_2(C_2H_3O_2) + KOH = \underset{\text{Propyl alcohol}}{CH_3.CH_2.CH_2OH} + KC_2H_3O_2$$

It must of course be remembered that the purity of the alcohol obtained depends upon that of the haloid paraffin employed. It should also be noted that the iodides react more readily than the bromides, and those than the chlorides.

3. Another method of producing alcohols, which has been already illustrated, is that in which an olefine is dissolved in H_2SO_4, and the resulting salt boiled with water. In the case of propylene and the higher olefines, the secondary alcohols are frequently formed.

4. Since primary alcohols yield aldehydes and acids by oxidation (see p. 96), it might be expected that reduction of these substances would produce the reverse action. Actually, if aldehydes, and either the chlorides or anhydrides of the acids, are reduced, *e.g.* by sodium amalgam in acid solution, they give alcohols—

$$\underset{\text{Propionic aldehyde}}{CH_3.CH_2.CHO} + H_2 = \underset{\text{Propyl alcohol}}{CH_3.CH_2.CH_2OH}$$

$$\underset{\text{Acetic anhydride}}{(CH_3.CO)_2O} + 2H_2 = \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} + \underset{\text{Acetic acid}}{CH_3.COOH}$$

$$\underset{\text{Acetyl chloride}}{CH_3.COCl} + 2H_2 = CH_3.CH_2OH + HCl$$

Ketones, the first oxidation products of secondary alcohols (see p. 96), also yield alcohols when similarly treated—

$$\underset{\text{Acetone}}{(CH_3)_2CO} + H_2 = \underset{\text{Iso-propyl alcohol}}{CH_3.CH(OH).CH_3}$$

5. When primary amines (see p. 163) are acted upon by nitrous acid alcohols are formed. This reaction is, however, only simple in the case of methylamine and ethylamine. Higher amines yield a mixture of primary and secondary alcohols—

$$CH_3.CH_2NH_2 + HNO_2 = CH_3.CH_2OH + N_2 + H_2O$$

6. A special reaction for producing tertiary alcohols is given under the butyl alcohols (p. 100).

Properties.—The lower members of the alcohol series are colourless, limpid liquids miscible with water; the intermediate members are oily liquids; while the highest, such as cetylic, cerylic, and melissic alcohols, are solids. As their molecular weight increases they become less soluble in water. The boiling points of alcohols of similar structure increase about 19° C. for every addition of CH_2 to the molecule; primary alcohols boil at a higher temperature than the isomeric secondary alcohols, and these boil higher than the corresponding tertiary. It has been already shown that methyl and ethyl alcohols act in many cases as if they were hydroxides of organic radicles, and their behaviour in this respect with acids and metals is typical of their higher homologues.

Primary, secondary, and tertiary alcohols show very characteristic differences when oxidised, and these differences serve for their diagnosis.

Diagnosis of Alcohols.—The three classes of alcohols may be differentiated in two different fashions: (1) by a study of their oxidation products, and (2) by the action of nitrous acid on the *nitro-paraffins* producible from them.

The first method is tedious, because it requires as a rule the quantitative examination of the substances produced; but it has the advantage of throwing very considerable light on the constitution of the alcohols. Shortly stated, **primary alcohols** yield, on oxidation, first an *aldehyde*, and then an *acid*, *both* of which contain the *same number of carbon atoms* as the alcohol—

$$C_2H_5OH + O = \underset{\text{Acetaldehyde}}{C_2H_4O} + H_2O$$

$$C_2H_4O + O = \underset{\text{Acetic acid}}{C_2H_4O_2}$$

If the alcohol is **secondary,** the first result of oxidation is the formation of a *ketone*, which, on further action, yields an acid or acids containing *less carbon atoms* than the original compound. Thus:

$$\underset{\text{Iso-propyl alcohol}}{(CH_3)_2CHOH} + O = \underset{\text{Acetone}}{(CH_3)_2CO} + H_3O$$

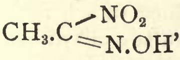
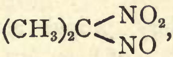
$$\underset{\text{Acetone}}{(CH_3)_2CO} + 2O_2 = \underset{\text{Acetic acid}}{CH_3.COOH} + CO_2 + H_2O$$

In the second reaction formic acid is first formed, but breaks up into CO_2 and H_2O. The simplest radicle usually remains attached to the C of the CHOH group.

Finally, a **tertiary alcohol** gives neither aldehydes nor ketones with the same number of carbon atoms, but acids or ketones containing a less number. Thus tri-methyl carbinol yields, first, formic acid and acetone, $(CH_3)_2CO$, which latter yields acetic acid $CH_3.COOH$, H_2O, and CO_2.

The second method, due to Meyer and Locher, is more readily applied, but is not applicable to alcohols which contain more than 8 carbon atoms.

Process.—First transform the alcohols into the corresponding iodides by means of concentrated hydriodic acid. Then introduce equal quantities of dry silver nitrite and fine sand into a small distillation flask, provided with a side tube 10 cm. long, and add a little of the alcoholic iodide. When the reaction is over, heat over a small flame and collect the distillate in a test-tube. Mix this distillate with three times its volume of a solution of KNO_2 in strong KOH solution, and shake well. Next add cautiously dilute H_2SO_4, and according as the resultant fluid is dark red, dark blue, or colourless, there was originally present a primary, secondary, or tertiary alcohol.

This reaction depends upon the formation of nitro-paraffins by the action of $AgNO_2$ upon the alcoholic iodides. If the nitro-paraffin formed is a primary compound, it yields with nitrous acid a nitrolic acid (p. 111), *e.g.* $CH_3.CH_2(NO_2)$ gives  $CH_3.C\begin{matrix}\nearrow NO_2\\ \searrow\!= N.OH\end{matrix}$, the alkaline salts of which possess a dark red colour; a secondary nitro-paraffin gives a pseudo-nitrol, *e.g.* $(CH_3)_2CH(NO_2)$ gives  $(CH_3)_2C\begin{matrix}\nearrow NO_2\\ \searrow NO\end{matrix}$, which gives a dark blue colouration when in solution; while a tertiary nitro-compound does not react at all.

Experiment 14.—Try the second method, identifying the kind of alcohol radicle present in ethyl iodide, iso-butyl iodide, and tertiary butyl iodide respectively.

Propyl Alcohols, $C_3H_7.OH$.—Two isomers.

n-Propyl Alcohol, $CH_3.CH_2.CH_2OH$, *ethyl carbinol.*—

After repeated failures, the presence of this alcohol has been conclusively demonstrated in fusel oil, so that it is one product of the fermentation of different sugars. It may be prepared artificially by the reduction of propionic aldehyde or propionic acid. It is now obtained in quantity by fractionally distilling the "feints" from the rectification of crude alcohol. The "feints" is a mixture of different propyl, butyl, and amyl alcohols. As it is impossible to separate perfectly the two propyl alcohols by such fractionation, they are next converted into the corresponding bromides, which are separated by distillation, and retransformed into the alcohols in the ordinary manner (see p. 94).

Properties.—Propyl alcohol is a colourless, refractive liquid, of b.p. 97·4°, sp. gr. 0·8088 at $\frac{15^\circ}{15^\circ}$ C. Its odour resembles that of ordinary alcohol. It is miscible in all proportions with water, but separates out on addition of $CaCl_2$ or other salts, which fact distinguishes it from ethyl alcohol. When oxidised it gives the corresponding aldehyde and acid.

Secondary Propyl Alcohol, $(CH_3)_2CHOH$, *iso-propyl alcohol, di-methyl carbinol,* is found in the "feints" obtained in rectifying spirit. It may be prepared by the reduction of acetone, and from iso-propyl iodide, or from propylamine by general methods (pp. 94, 95).

Process.—It is usually prepared by heating iso-propyl iodide with lead hydroxide and water, in a flask provided with a reflux condenser. The product is distilled, and the distillate dehydrated by potash.

Properties.—Secondary propyl alcohol is a colourless mobile liquid, b.p. 83° (cor.), sp. gr. 0·791 at $\frac{15^\circ}{15^\circ}$. It has a slight alcoholic odour, is miscible with water, alcohol, and ether, and is separated from its aqueous solution by KOH. It forms several hydrates with water. On oxidation it yields acetone, and then formic and acetic acids.

Constitution of the Propyl Alcohols.—The constitution of normal propyl alcohol follows from its formation from propionic acid and propionic aldehyde. It will be shown later (p. 194) that carboxyl acids, *i.e.* acids which are characterised by the group —CO.OH may be formed by the successive introduction of halogen and —CN radicles in place of the OH group of an alcohol, and final saponification of the cyanogen derivative. If, then, the position in the molecule of such a —COOH group is known, when it is reduced the position of the —CH_2OH is also known. Now, the COOH group in propionic acid can only take one possible position in the hydrocarbon from which it is derived, viz. ethane, $CH_3.CH_3$, can only yield $CH_3.CH_2.COOH$; hence on reduction normal propyl alcohol, $CH_3.CH_2.CH_2OH$, is formed.

The constitution of secondary propyl alcohol, $CH_3.CH(OH).CH_3$, follows from the fact that on oxidation it yields acetone, for which the formula $CH_3.CO.CH_3$ is well proved.

Butyl Alcohols, C_4H_9OH.—Of these alcohols there are four isomers, all known: two are primary alcohols, one is secondary, and one tertiary.

1. **Normal Butyl Alcohol,** $CH_3.CH_2.CH_2.CH_2OH$, *propyl carbinol*, is found in the heavy oils from brandy, and in the "feints" before mentioned. It is a product of the fermentation of glycerin by certain bacteria and also by a schizomycetes, and can be synthetically prepared by reduction of butyric aldehyde or butyric acid.

Properties.—Butyl alcohol is an oily, colourless, highly refractive liquid, b.p. 117° C. (cor.), sp. gr. 0·8233 at $\frac{0^\circ}{0^\circ}$. It has a peculiar odour, and its vapour excites coughing. It is moderately soluble in water, and separated from solution by $CaCl_2$. It yields butyric acid on oxidation.

2. **Iso-butyl Alcohol,** $(CH_3)_2CH.CH_2OH$, *iso-propyl carbinol*, *fermentation butyl alcohol*, is usually obtained from the feints. It is also found in combination in Roman chamomile oil, and is produced by the fermentation of sugar by the *Bacillus butylicus.*

Properties.—Iso-butyl alcohol is a colourless liquid which smells like fusel oil, b.p. 108°, sp. gr. 0·807 at $\frac{15^\circ}{15^\circ}$.

3. **Secondary Butyl Alcohol,** $CH_3.CH_2.CH.OH.CH_3$, *methyl-ethyl carbinol*, is usually prepared from secondary butyl iodide. It was first obtained from erythrite by reduction

with HI to secondary butyl iodide, from which the alcohol can be prepared by the ordinary method.

Properties.—It is a colourless liquid, b.p. 99° C., sp. gr. 0·827 at $\frac{0^\circ}{}$; has a strong but pleasant odour and burning taste.

4. **Tertiary Butyl Alcohol,** $(CH_3)_3COH$, *tri-methyl carbinol*, is produced by the reaction which led to the discovery of tertiary alcohols, namely, that of zinc methide upon acetyl chloride. The reaction is complicated, but may be represented thus—

(i.) $CH_3.COCl + 2Zn(CH_3)_2 = (CH_3)_3.COZnCH_3 + CH_3ZnCl$

(ii.) $(CH_3)_3.COZnCH_3 + 2H_2O = (CH_3)_3COH + Zn(OH)_2 + CH_4$

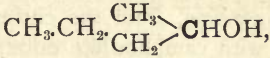
Properties.—Tertiary butyl alcohol forms, when anhydrous, colourless prismatic needles, m.p. 25° C., b.p. 83° C., sp. gr. 0·7836 at $\frac{15^\circ}{15^\circ}$. When fused it is an oily liquid with a camphor-like odour. It forms a hydrate, $C_4H_{10}O_2.H_2O$, which boils at 80°.

Constitution of the Butyl Alcohols.—The constitutions of n-butyl alcohol and iso-butyl alcohol may be deduced from their respective formation from butyric and iso-butyric acids, which are themselves formed from propyl and iso-propyl alcohols respectively, by transforming them into the corresponding cyanides (nitriles) and saponifying those. We may infer that the constitution of secondary butyl alcohol is represented by the formula $CH_3.CH_2.CH(OH).CH_3$, from the fact that on oxidation it yields methyl-ethyl ketone; and, finally, the formula for tertiary butyl alcohol can only be, by elimination of the others, $(CH_3)_3COH$.

Amyl or Pentyl Alcohols, $C_5H_{11}OH$.—According to ordinary chemical formulæ, there are theoretically eight possible isomers. Two, however, of these possess an **asymmetric carbon atom,** *i.e.* a carbon atom which is attached to four different radicles. Such an atom is indicated in the formulæ by thick type.

Now, when a compound contains such a carbon atom, it has been found that it usually occurs in two forms, which possess different optical properties. One of the forms rotates a ray of polarised light to the right, and the other to the left, or they are said to be dextro- and lævo-rotatory respectively. When such compounds are produced in a reaction in equal quantities, the resultant substance will be optically inactive, and it is usually difficult to separate it into the two varieties. If more than one asymmetric carbon atom is present, the number of isomers is still further increased. Amongst examples of this phenomenon which will be met with, may be mentioned lactic, malic, and tartaric acids and the sugars.

Three of the amyl alcohols are derived from pentane, four from iso-pentane, and one from tetra-methyl-methane; the last is unknown.

(1) **n-Amyl Alcohol,** $CH_3.(CH_2)_3.CH_2OH$, *butylcarbinol*, b.p. 137°; (2) **Methyl-propyl Carbinol,**  $CH_3.CH_2.\begin{matrix}CH_3\\CH_2\end{matrix}>CHOH$, b. p. 119°; and (3) **Di-ethyl Carbinol,** $(CH_3.CH_2)_2CHOH$, b. p. 117°; are derivatives of pentane.

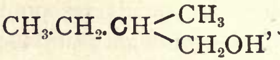
All three are liquids, and the first occurs in fusel oil. The second is noteworthy because it contains an asymmetric carbon atom, and although optically inactive as ordinarily prepared, if ordinary mould (*Penicillium glaucum*) is grown in it, an alcohol which is optically active (lævo-rotatory) remains.

The following alcohols are derived from iso-pentane:—

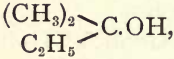
Commercial or **Fermentation Amyl Alcohol,** "*iso-amyl alcohol," or fusel oil,* is a mixture of inactive and active alcohols, and is the product of the fermentation of various saccharine materials. The alcohols may be separated by fractional crystallisation of the barium salts of the corresponding amyl sulphates.

The crude alcohol is a colourless liquid, b.p. about 131°, sp. gr. 0·810 at $\frac{20°}{4°}$. It has a powerful and penetrating smell and a burning taste, and its vapour, when inhaled, produces coughing, giddiness, and headache. Its toxic effect is much greater than that of ordinary alcohol; hence the evil effects which follow from drinking impure spirits. It is optically active, though in a varying degree.

Inactive Amyl Alcohol, $(CH_3)_2CH.CH_2.CH_2OH$, *iso-butyl carbinol*, is present in Roman chamomile oil and in iso-amyl alcohol. It is a liquid, b.p. 131·5° C. (cor.), sp. gr. 0·8135 at $\frac{15^\circ}{15^\circ}$. It is optically inactive.

Active Amyl Alcohol,  $CH_3.CH_2.CH\begin{matrix}\diagup CH_3 \\ \diagdown CH_2OH\end{matrix}$, *secondary butyl-carbinol,* from iso-amyl alcohol, has probably not been obtained pure; it boils at 127–128° C., and its sp. gr. at $\frac{15^\circ}{15^\circ}$ is 0·815. As prepared it is lævo-rotatory, but if treated in dilute solution with *Penicillium glaucum,* it becomes dextro-rotatory.

Methyl-iso-propyl Carbinol, $(CH_3)_2CH.CH(OH).CH_3$, from the corresponding ketone, is a fragrant-smelling liquid, b.p. 113°, sp. gr. 0·833 at $\frac{0^\circ}{}$.

Tertiary Amyl Alcohol,  $\begin{matrix}(CH_3)_2 \\ C_2H_5\end{matrix}\!>\!C.OH$, *di-methyl-ethyl carbinol,* from the corresponding iodide, is a colourless liquid with camphor-like odour, sp. gr. 0·814 at $\frac{15^\circ}{15^\circ}$, b.p. 102, which solidifies to a solid, m.p. −12°.

CHAPTER XIV.

ETHERS.

THE constitution of the ethers may be shortly expressed by saying that they bear the same relation to alcohols that oxides of monad metals do to their hydroxides. Thus—

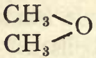
$$K_2O + H_2O = 2KOH$$

and by suitable means the reaction below can also be accomplished—

$$\underset{\text{Ethyl oxide}}{(C_2H_5)_2O} + H_2O = 2C_2H_5OH$$

Ethers are therefore the oxides of the alkyl (alcoholic) radicles, or can be considered also as anhydrides of the alcohols.

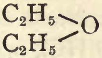
Ethers can be either **simple** or **mixed**; *i.e.* both the radicles attached to the oxygen atom may be identical, forming simple ethers, or they may be different, and then mixed ethers are formed. So, *e.g.*, the following are simple ethers—



$\begin{matrix}CH_3\\CH_3\end{matrix}>O$

Di-methyl ether,
methyl ether

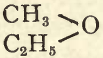
and



$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$

Di-ethyl ether,
ethyl ether

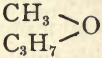
while as examples of mixed ethers may be cited—



$\begin{matrix}CH_3\\C_2H_5\end{matrix}>O$

Methyl-ethyl ether

and



$\begin{matrix}CH_3\\C_3H_7\end{matrix}>O$

Methyl-propyl ether

Besides the terms "simple" and "mixed ethers," the expression **compound ether** is frequently used. Now, a compound ether is in reality a salt in which an organic radicle takes the place of a metal, and is so termed because, while an ether may be looked upon as derived from water in which both hydrogen atoms are replaced by alkyl radicles, in a compound ether one hydrogen atom is replaced by an alkyl group and the other by an acid radicle. Thus ethyl nitrate, $C_2H_5NO_3$, may be written $C_2H_5O(NO_2)$. It is now becoming customary to term compound ethers **esters.** The esters of inorganic acids will be considered after the ethers, and those of the organic acids after the acids concerned.

ETHERS.

The preparation and properties of the series will find most complete exemplification when we discuss ordinary ether, di-ethyl ether, although the di-methyl derivative will be first mentioned.

Di-methyl ether, $(CH_3)_2O$, *methyl oxide*, *methyl ether*, is formed when 20 parts of H_2SO_4 and 13 parts of methyl alcohol are heated together to 140°. The gas evolved is washed through caustic soda, and may then be passed into strong sulphuric acid, which absorbs 600 times its own volume of it to form the compound $(CH_3)_2O.H_2SO_4$. This can be kept without change, and if dropped into an equal volume of water the ether is evolved, and may be dried over $CaCl_2$ and collected.

Properties.—Methyl ether is a gas that is condensible by pressure to a liquid, b.p. $-24°$, which may be used for producing artificial cold. The gas is not very soluble in water, but readily in alcohol and ether. It forms with dry HCl the compound $(CH_3)_2O.HCl$, which boils at -2°; and it forms substitution products when acted on by chlorine.

Ether or Di-Ethyl Ether, $(C_2H_5)_2O$, *ethyl oxide, ethyl ether, "sulphuric ether"* (Æther, B.P.). (*1) Ether is usually prepared by what is termed the "continuous" process, by heating alcohol with sulphuric acid to 140°. The reaction *may* be represented by the equation—

$$2C_2H_5OH + H_2SO_4 = (C_2H_5)_2O + H_2O + H_2SO_4$$

but it really takes place in two stages. There is first formed an acid sulphate of ethyl, which when boiled with alcohol yields ether and the acid—

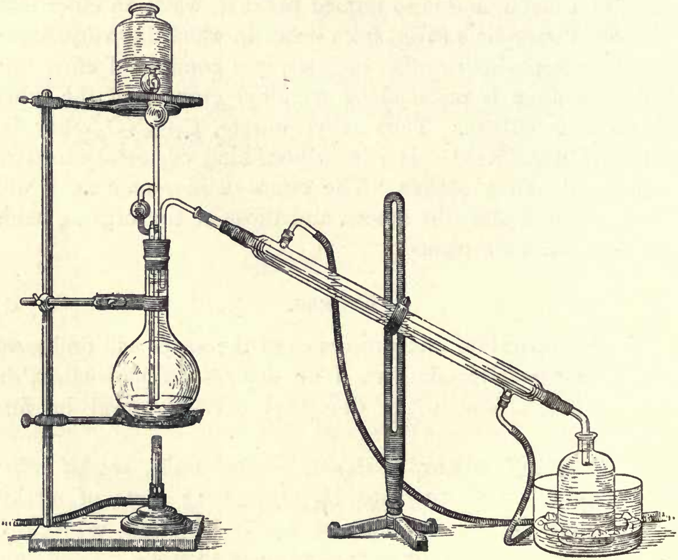


FIG. 36.

$$\text{(i.)} \quad C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O$$

$$\text{(ii.)} \quad C_2H_5SO_4H + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

† *Process.*—Carefully mix 9 parts of strong H_2SO_4 with 5 parts of 90 per cent. rectified spirits of wine, and bring the mixture into a flask provided with a well-fitting cork bored with 3 holes (Fig. 36).

Through one of the holes is passed a stoppered funnel, in another is fitted a bent tube which is joined to a condenser, and through the third is passed a straight glass tube that dips into the liquid and in which a thermometer is suspended. The mixture of alcohol and acid given boils at about 140°, and at that temperature ether distils over along with water and a little alcohol. As the reaction proceeds alcohol is dropped in from the funnel to take the place of that which has been decomposed, and the reaction would go on continuously if the alcohol were anhydrous, and no by-reactions occurred. Actually, however, water accumulates in the flask and weakens the acid, so that less alcohol is acted on as time passes; also a certain amount of the acid itself becomes reduced, SO_2 being evolved, so that after about 35 parts of alcohol have been used, it is best to start the operation afresh.

Purify the ether by shaking with milk of lime or NaOH to free it from SO_2, and distil from the water-bath. Pour the distillate on to fused $CaCl_2$, allow it to stand for some time, and again rectify by distillation. This treatment frees it from most of the water and alcohol which is mixed with it, leaving it sufficiently pure for most purposes.

Purification.—If required pure, wash it repeatedly with water till free from alcohol, as shown by the iodoform test, dry first over $CaCl_2$, and then over slices of sodium till no more hydrogen is evolved, and finally distil from the water-bath.

Ether is also produced (*2) when ethyl iodide acts upon sodium or potassium ethylate—

$$C_2H_5I + C_2H_5ONa = (C_2H_5)_2O + NaI$$

and also (*3) by heating dry silver oxide with ethyl iodide—

$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI$$

The two last processes are not of great importance for its preparation, except in so far as they throw light upon the *constitution of ether*, and show that both its alkyl groups are directly united to the oxygen atom.

Properties.—Pure ether is a colourless, mobile, neutral liquid, with somewhat pleasant odour and burning taste. Its sp. gr. is 0·7201 at $\frac{15°}{15°}$; it is exceedingly volatile; its b.p. is 34·6°, and it freezes to a solid, m.p. $-117°$. It is very inflammable, burning with a luminous flame, and its vapour forms a strongly explosive mixture with air. It is slightly soluble in water, readily in alcohol, and 100 parts of ether dissolve about 3 parts of water. Ether is a very useful solvent for many inorganic and organic substances, such as I, Br, S, P, fats, resins, and oils, and is largely used as an anæsthetic.

It is oxidised in presence of air by platinum black, heated Pt sponge, or red-hot Pt wire, with the formation of acetic and formic acids, CO_2, and aldehyde; HNO_3 and chromic acid also oxidise it; and ozone acts on it very violently—the explosive compound **ether peroxide** is said to be formed in the reaction. P_2O_5 has *no action* upon ether, but P_2S_5 forms the corresponding sulphide, $(C_2H_5)_2S$. Chlorine acts on it violently; thus, if a little ether is poured into a jar of chlorine an explosion occurs; if, however, suitable precautions are taken, substitution compounds are formed; bromine acts much more gently, and iodine only slightly. Sodium, ammonia, and the alkalis do not affect ether. *Dilute* H_2SO_4, HCl, or PCl_5 do not act on it when cold, but if it is heated in closed tubes with very dilute H_2SO_4 it re-forms alcohol. Concentrated HI, HCl, or PCl_5, and H_2SO_4 form ethyl esters when warmed with it—

$$(C_2H_5)_2O + 2HCl = 2C_2H_5Cl + H_2O$$
$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3$$
$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5SO_4H + H_2O$$

If the HI is cold, a molecule each of the alcohol and the alkyl iodide is formed. Ether combines with many salts to form molecular compounds; *e.g.* $(C_2H_5)O.SnCl_4$, $(C_2H_5)_2O.SbBr_3$, and $3(C_2H_5)_2O.HgBr_2$.

GENERAL REMARKS ON ETHERS.

The methods given for the production of ether are of general application.

1. By abstraction of the elements of water from two molecules of an alcohol by the action of H_2SO_4. This method is applicable also for the production of mixed ethers; thus if methyl alcohol is dropped into heated ethyl hydrogen sulphate, methyl-ethyl ether is formed—

$$C_2H_5SO_4H + CH_3OH = C_2H_5OCH_3 + H_2SO_4$$

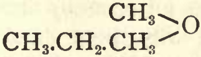
2. By the action of haloid paraffins upon ethylates—

$$C_2H_5ONa + CH_3I = C_2H_5OCH_3 + NaI$$

3. From dry silver oxide and alkyl iodides. The last methods serve for the formation of both simple and mixed ethers.

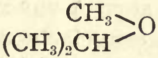
Properties.—Most of the ethers are colourless liquids, although the highest members are solids. They resemble ordinary ether in their properties, being neutral in reaction and almost insoluble in water, although readily soluble in alcohol, and boil at lower temperatures than the isomeric alcohols. The chemical reactions they undergo have been thoroughly illustrated by ethyl ether, and support the conclusion that they are oxides of organic radicles.

The mixed ethers afford us the first example of a form of isomerism termed **metamerism**. Thus the following ethers are **metameric**, *i.e.* are **metamers** :—



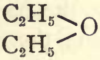
$\begin{matrix}CH_3\\CH_3.CH_2.CH_3\end{matrix}\!\!>\!O$;

Methyl propyl ether



$\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\!\!>\!O$; and

Methyl iso-propyl ether



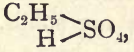
$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O$

Compounds are termed metameric when their isomerism is caused by the linkage together of different groups (which, though individually unequal, give the same sum-total of atoms) by means of a polyvalent element, in this case oxygen.

CHAPTER XV.

COMPOUND ETHERS, ETHEREAL SALTS, OR ESTERS, OF THE MINERAL ACIDS.

We have already had reason to define the meaning of the term "ether," and to explain that ethers proper differ from compound ethers in that they contain only hydrocarbon radicles attached to oxygen, while in the latter, one of the radicles is an acid residue. Perhaps the term "compound ether," or, better, an "ester," may be best defined as a salt in which alcoholic radicles have been substituted for the typical hydrogen of an acid. Consequently, if an acid be polybasic, we may have acid or neutral salts or esters, or, also, we can have salts which are partly metallic and partly alcoholic ; thus—

HNO_3 will yield $C_2H_5NO_3$
H_2SO_4 ,,  $\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_4$, $(C_2H_5)_2SO_4$, and  $\begin{matrix}C_2H_5\\K\end{matrix}\!>\!SO_4$

and organic acids give similar results.

Summing up, it may be said, in short, that if an alcohol is the hydroxide and an ether the oxide of a hydrocarbon radicle, an ester is formed by the combination of such a radicle with an acid. It is convenient to study here those formed with inorganic acids; those derived from organic acids will be studied as occasion serves.

ESTERS OF NITROUS ACID.

The usual formula assigned to nitrous acid is HONO, in which the hydrogen atom is united to nitrogen by means of oxygen; there is no reason, however, why there should not be an acid isomeric with it which might be represented by the formula $H.NO_2$, in which the hydrogen is directly united to the nitrogen atom, and actually there is a well-known class of organic compounds which appear to be derived from such an acid.

The derivatives of the first acid are termed esters of nitrous acid, while those of the second are generally called **nitro-compounds**; and the two classes are sharply differentiated from each other by their different stability and action towards reducing agents and dilute alkalis.

Methyl Nitrite, CH_3ONO, formed by the action of HNO_3 and copper upon methyl alcohol, is an agreeable-smelling gas condensible to a liquid, b.p. $-12°$.

Ethyl Nitrite, C_2H_5ONO, is formed (*1) by the action of HNO_3 on alcohol; the reaction is violent, part of the acid is reduced by part of the alcohol, and the N_2O_3 thus formed esterifies the remainder—

$$2C_2H_5OH + N_2O_3 = 2C_2H_5NO_2 + H_2O$$

Obtained in this manner it always contains aldehyde; this can be avoided (2) by passing N_2O_3 into alcohol, or (3) by acting with dilute H_2SO_4 and $NaNO_2$ upon alcohol.

†*Process.*—Dissolve 34·5 grams $NaNO_2$ in 120 c.c. H_2O, and cool below 0°. Add 13·5 grams H_2SO_4 to a mixture of 32 c.c. rectified spirit and 32 c.c. H_2O, then cool and dilute to 120 c.c. Slowly add this acid mixture, by means of a drop-funnel, to the solution of $NaNO_2$. Separate the ethyl nitrite formed, wash with ice-cold water, and dry over ignited K_2CO_3.

Properties.—Ethyl nitrite is a colourless, limpid liquid with a refreshing ethereal odour, b.p. 18°, sp. gr. 0·9 at $\underline{15^\circ}$. It is slightly soluble in water, readily in alcohol. If pure it is stable, but impure or wet it readily decomposes with liberation of NO; glycerin added to its alcoholic solution prevents this decomposition. Reducing agents liberate NO, and alkalis saponify it—

$$C_2H_5NO_2 + NaOH = C_2H_5OH + NaNO_2$$

This decomposition of ethyl nitrite is a characteristic example of the manner in which all compound ethers or esters break up on heating with water or dilute alkalis or acids, and is termed "saponification," though perhaps the better term would be "hydrolysis;" it is the reverse of the process of forming esters from an acid and an alcohol. The term "saponification" was originally applied to the decomposition of fats by alkalis (see Soaps, p. 153).

Spiritus Ætheris Nitrosi is an impure form of ethyl nitrite used in medicine. Formerly it was prepared by acting upon HNO_3 with an excess of alcohol, and contained little nitrous ether, and was called "sweet spirit of nitre." It is made now for pharmaceutical purposes as follows: gradually add 2 fluid ozs. of H_2SO_4 to a pint of rectified spirit; then carefully add 2½ ozs. of HNO_3, and pour the acid mixture into a retort which contains 2 ozs. of No. 25 copper wire. Fit the retort with a thermometer, attach to it a condenser, and distil the contents at from 76° to 79° (the temperature must not exceed 82°), until 12 ozs. have passed over. Cool the contents of the retort, add ½ oz. more HNO_3, and distil off 2 ozs. more. Dilute this distillate with about 2 pints of spirit, so that it will yield not more than seven, or less than five, times its own volume of NO, measured at 15·5° and 760 mm., when decomposed by $FeSO_4$ and H_2SO_4 according to the following reaction :—

$$2C_2H_5NO_2 + 2FeSO_4 + H_2SO_4 = 2C_2H_5OH + Fe_2(SO_4)_3 + 2NO$$

This volume of gas corresponds to 2–3 per cent. of the nitrite. This official solution should have a specific gravity of about 0·840 to 0·845, and should not effervesce, or only slightly so, when shaken with $NaHCO_3$.

Amyl Nitrite, $C_5H_{11}NO_2$, is obtained as a yellowish liquid, b.p. 99°, sp. gr. 0·9, by acting upon iso-amyl alcohol with KNO_2 and dilute H_2SO_4.

In a somewhat impure form it finds considerable use in medicine as **amyl nitris**, B.P., which is prepared from amyl alcohol, boiling at 132°, by distilling it carefully with an equal volume of HNO_3 in a large retort. The distillate is collected up to 100°, washed with aqueous potash, separated, and then *slowly* distilled ; that portion which comes over between 96° and 100° is collected as amyl nitrite.

It possesses a disagreeable, stupefying odour, and its vapour when inhaled causes dilation of the blood-vessels, and consequent rush of blood to the head and flushing. It has found use in angina pectoris, asthma, etc. If of good quality, about 70 per cent. should distil over between 90° and 100°.

Nitro-methane, CH_3NO_2, produced by acting upon silver nitrite with methyl iodide, is a mobile liquid, b.p. 101°.

Nitro-ethane, $CH_3.CH_2NO_2$, is produced (*1) along with some ethyl nitrite by heating ethyl iodide with $AgNO_2$—

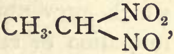
$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI$$

(*2) It is also formed by distilling ethyl hydrogen sulphate with $NaNO_2$, the yield being, however, small—

$$C_2H_5SO_4H + NaNO_2 = C_2H_5NO_2 + NaHSO_4$$

These methods are the first examples of two processes generally useful in preparing esters.

Properties.—Nitro-ethane is a colourless, refractive oil with a pleasant ethereal smell, b.p. 114°, sp. gr. 1·0561 at $\frac{15°}{15°}$. It is reduced by nascent hydrogen to ethylamine,

$C_2H_5NH_2$; heated with HCl, sp. gr. 1·14, it forms hydroxylamine and acetic acid. Nitro-ethane is slightly acid in its properties, so that alcoholic soda forms the Na salt, $CH_3.CHNaNO_2$. If it is mixed with KOH and KNO_2, and H_2SO_4 then slowly added, *ethyl nitrolic acid*,  $CH_3.CH\begin{smallmatrix}\diagup NO_2\\ \diagdown NO\end{smallmatrix}$, is produced, of which the alkaline salts are red (see p. 97).

Constitution.—There appears little doubt that nitro-paraffins possess the constitution already assigned to them (p. 108). The fact that nitro-ethane yields on reduction the compound $C_2H_5NH_2$, for which there is abundant evidence that the nitrogen atom is linked to carbon, supports the idea that in other nitro-compounds nitrogen is also so combined. It also resists saponification—another argument in favour of such a fact, since all esters, in which the alkyl radicles are apparently linked to the carbon atom by means of oxygen, are readily decomposed.

The following more complex "nitro-compounds" should be noted.

Nitroform, $CH(NO_2)_3$, *tri-nitro-methane*, is a colourless thick oil, forming white crystals below 15°. It explodes when heated, and acts as a strong acid, the H of the CH group having an acid character due to the influence of the nitro groups.

Nitro-chloroform or **Chloropicrin**, $C(NO_2)Cl_3$, *tri-chlor-nitro-methane*, is obtained by distilling alcohol with a mixture of NaCl, KNO_3, and H_2SO_4, or most readily by acting upon picric acid with bleaching powder. It is a colourless liquid, b.p. 112°, sp. gr. 1·69 at $\frac{0^\circ}{4^\circ}$. It has a pungent odour, and explodes when rapidly heated.

Esters of Nitric Acid.

Methyl Nitrate, CH_3ONO_2, may be prepared by distilling methyl alcohol with nitric acid, best in the presence of urea nitrate (see Ethyl Nitrate). It is a colourless liquid with an ethereal odour, slightly soluble in water, b.p. 65°, sp. gr. 1·2167 at $\frac{15^\circ}{15^\circ}$. When ignited it burns with a yellow flame; it explodes on being struck, and its vapour, when heated to 150°, explodes with tremendous violence.

Ethyl Nitrate, $C_2H_5ONO_2$, is formed by the action of HNO_3 on ethyl alcohol in the presence of some substance which prevents the reduction of the acid and consequent formation of ethyl nitrite. Urea answers this purpose well, any nitrous acid which may be formed being decomposed at once, according to the reaction—

$$CO(NH_2)_2 + 2HNO_2 = 3H_2O + CO_2 + 2N_2$$

The reaction between the alcohol and acid is—

$$C_2H_5OH + HNO_3 = C_2H_5ONO_2 + H_2O$$

This is a typical example of a general reaction for the formation of esters. The reaction is, however, never complete unless the water is removed from the sphere of action by some means, because it weakens the acid and also decomposes the ester, till a stage is arrived at when the decomposition and combination are equal.

Process.—It may be prepared as follows: Warm 80 grams HNO_3, sp. gr. 1·4, with urea nitrate; cool, and add to this 60 grams alcohol, sp. gr. 0·81, and 15 grams nitrate of urea, and distil to one-eighth of its volume. Wash well with water, and dry over $CaCl_2$ or K_2CO_3.

Properties.—Ethyl nitrate is a colourless, mobile liquid, with a pleasant smell and sweet taste, b.p. 86°, sp. gr. 1·112 at $\frac{15\cdot5^\circ}{}$. It burns with a white flame, and its vapour, when strongly heated, explodes violently. When reduced by tin and HCl, hydroxylamine is produced. Water and alkalis, the latter readily, decompose it into the alcohol, and acid or salt of the acid respectively—

$$C_2H_5ONO_2 + NaOH = C_2H_5OH + NaNO_3$$

ESTERS OF HYDROGEN SULPHIDE, OR THIO-ALCOHOLS AND THIO-ESTERS.

Just as the alcohols and ethers may be considered as derived from water, by the replacement of hydrogen by alkyl groups, so the thio-alcohols and thio-ethers may be looked upon as bearing a similar relation to hydrogen sulphide.

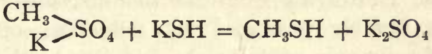
$$\begin{array}{llll} & HOH \text{ gives } & C_2H_5OH \text{ and } & (C_2H_5)_2O \\ \text{and } & HSH \quad ,, & C_2H_5SH \quad ,, & (C_2H_5)_2S \end{array}$$

Since hydrogen sulphide, however, possesses acid properties, the thio-alcohols and ethers may also be looked upon as its ethereal salts.

THIO-ALCOHOLS OR MERCAPTANS; *i.e.* ACID ESTERS OF HYDROGEN SULPHIDE.

Of these bodies the simplest is—

Methyl Mercaptan, CH_3SH, or *methyl sulphydrate,* which occurs in human excrement, and can be prepared by distilling potassium methyl sulphate with potassium hydrosulphide—



$$\genfrac{}{}{0pt}{}{CH_3}{K}\!\!>\!SO_4 + KSH = CH_3SH + K_2SO_4$$

It is a light, colourless liquid with an unpleasant odour (?),[1] b.p. 21°.

Mercaptan, or **Ethyl Mercaptan,** C_2H_5SH, *thio-alcohol,* may be formed (*1) by distilling potassium ethyl sulphate with KSH—

$$C_2H_5SO_4K + KSH = C_2H_5SH + K_2SO_4$$

The student may note that this reaction is quite analogous in character to saponification by KOH. (*2) The mercaptan is also produced when chlor- or iodo-methane is acted upon by KSH (compare Formation 1 of Alcohols, p. 94)—

$$C_2H_5I + KSH = C_2H_5SH + KI$$

Properties.—Ethyl mercaptan is a very mobile, colourless liquid, b.p. 36·5°, and sp. gr. 0·8391 at $\frac{20^\circ}{4^\circ}$. It possesses a very strong garlic-like odour (?) and an unpleasant taste. It is almost insoluble in water, but soluble in alcohol and ether. It burns with a pale blue flame, and has a neutral reaction.

---

[1] It has recently been stated that neither the mercaptans nor the alkyl sulphides possess (if perfectly pure) the unpleasant smell usually attributed to them.

When a drop of it is exposed on a glass rod and agitated in the air it becomes solid. It forms metallic compounds more readily than does alcohol; these are analogous to the alcoholates, and are called mercaptides. Thus mercaptan acts with violence upon the oxide and salts of mercury, forming the compound $(C_2H_5S)_2Hg$, mercury mercaptide; hence its name (*mercurio captans*). If mercaptan is treated with potassium, hydrogen is evolved and potassium mercaptide formed.

When mercaptan is oxidised by HNO_3, sp. gr. 1·4, it forms ethane sulphonic acid, $C_2H_5SO_3H$ (usually termed *ethyl* sulphonic acid), and if sodium mercaptide is exposed to air it forms the sodium sulphonate of ethane, $C_2H_5SO_3Na$. These reactions are of considerable interest in determining the constitution of the sulphonic acids (see p. 116).

General Remarks.—Besides the methods given, mercaptans are notably produced by reduction of the acid chlorides of sulphonic acids (*q.v.*); and also by the action of P_2S_5 on alcohols—

$$5C_2H_3OH + P_2S_5 = 5C_2H_5SH + P_2O_5$$

Properties.—The fatty mercaptans are mostly colourless or yellow liquids, which are almost or quite insoluble in water, possess a very disagreeable odour (?), and resemble mercaptan in their principal properties. A characteristic colour reaction (green) is obtained when a 1 per cent. solution of isatin in strong H_2SO_4 is shaken up with a mercaptan.

THIO-ETHERS, *i.e.* NEUTRAL ESTERS OF HYDROGEN SULPHIDE.

Ethyl Sulphide, $(C_2H_5)_2S$, will serve as an example of these, and is produced (*1) by the distillation of an alcoholic solution of K_2S and potassium ethyl sulphate—

$$2C_2H_5KSO_4 + K_2S = (C_2H_5)_2S + 2K_2SO_4$$

or (*2) when ethyl chloride is passed through a hot alcoholic solution of K_2S—

$$2C_2H_5Cl + K_2S = (C_2H_5)_2S + 2KCl$$

Other ethyl esters than C_2H_5Cl may be employed. Also (*3) when P_2S_5 acts upon ethers, replacing the oxygen—

$$5(C_2H_5)_2O + P_2S_5 = (C_2H_5)_2S + P_2O_5$$

and (*4) by the action of ethyl iodide upon potassium mercaptide (compare the formation of ether from ethyl iodide and an ethylate, p. 105)—

$$C_2H_5I + C_2H_5SK = (C_2H_5)_2S + KI$$

Properties.—Ethyl sulphide is a colourless, oily liquid with a disagreeable smell (?), b.p. 93° (cor.), sp. gr. 0·8368 at $\frac{20°}{4°}$. burns with a blue flame, and takes fire when poured into chlorine. It differs from mercaptan in having no action upon HgO. On oxidation with nitric acid, it yields either di-ethyl sulphoxide, $(C_2H_5)_2SO$, or di-ethyl sulphone, $(C_2H_5)_2SO_2$, according to the strength of acid employed. Like ordinary ether, it forms compounds with various metallic salts.

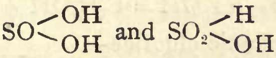
It reacts readily with C_2H_5I to form **tri-ethyl sulphine iodide**—

$$(C_2H_5)_2S + C_2H_5I = (C_2H_5)_3SI$$

a substance which crystallises in colourless plates, and is decomposed by moist silver oxide with the formation of **tri-ethyl sulphonium hydroxide,** $(C_2H_5)_3SOH$, which is strongly alkaline and caustic, liberates ammonia from its salts, precipitates many metallic hydroxides, redissolving $Al(OH)_3$, and forms neutral salts with acids.

ESTERS OF SULPHUROUS ACID.

Esters of sulphurous acid can be formed, which show that its compounds may exist in two isomeric forms (compare Nitrous Acid, p. 108), which correspond to symmetric and unsymmetric varieties respectively. Thus sulphurous acid may be represented by two formulæ—



$$SO\left<\begin{matrix}OH\\OH\end{matrix}\right. \text{ and } SO_2\left<\begin{matrix}H\\OH\end{matrix}\right.$$

Derivatives of the acid of the first formula are called esters of sulphurous acid, while those of the second are **sulphonic acids** or their derivatives.

It is quite sufficient to describe the ethyl derivatives in order to illustrate the characters of the two series.

Ethyl Hydrogen Sulphite, $\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_3$, is not known free, and its potassium salt, $C_2H_5KSO_3$, is also comparatively unstable.

Ethyl Sulphite, $(C_2H_5)_2SO_3$ is formed by adding an excess of absolute alcohol either to thionyl chloride or to sulphur chloride. The former reaction may be expressed thus—

$$\underset{\text{Thionyl chloride}}{SOCl_2} + 2C_2H_5OH = (C_2H_5O)_2SO + 2HCl$$

Properties.—It is a colourless, mobile liquid, which smells something like peppermint, b.p. 161°, and sp. gr. 1·085 at $\frac{16^{\circ}}{\cdot}$. It is soluble both in alcohol and ether, but not in water. Water or aqueous alkalis saponify it, more rapidly at a high temperature—

$$(C_2H_5O)_2SO + 2KOH = 2C_2H_5OH + K_2SO_3$$

Ethane Sulphonic Acid, or **Ethyl Sulphonic Acid,** $C_2H_5SO_2OH$, is formed (*1) by the oxidation of mercaptan with HNO_3, or of sodium mercaptide in air—

$$C_2H_5SH + O_3 = C_2H_5SO_2OH$$

(*2) The salts of this acid are formed when ethyl iodide acts upon a neutral sulphite, preferably an ammonium salt, at 120–150° in aqueous solution—

$$K.SO_2OK + C_2H_5I = C_2H_5SO_2OK + KI$$

Properties.—Ethyl sulphonic acid is a thick acid liquid, which crystallises in the cold, and decomposes on heating. It is not saponified by boiling with KOH solution, but on *fusing* with solid KOH it reacts in the ordinary manner—

$$C_2H_5SO_2OK + KOH = C_2H_5OH + KSO_2OK$$

PCl_5 forms the sulphonic chloride—

$$C_2H_5SO_2OH + PCl_5 = C_2H_5SO_2Cl + POCl_3 + HCl$$

which on reduction by nascent hydrogen yields mercaptan.

Constitution.—The formation of ethane sulphonic acid by oxidation of mercaptan is of great theoretical importance; it points clearly to the conclusion that the sulphur atom is linked to a carbon atom. Of course, it may be argued that there may have been a rearrangement of atoms; this idea is, however, excluded by the fact that the sulphonic chloride on reduction again yields mercaptan. The fact, too, that, unlike esters in which the alkyl group is attached to oxygen, the sulphonic acids are only saponified with difficulty (see Nitro-ethane, p. 111), also supports the unsymmetrical formula.

The **neutral esters** of the sulphonic acids are produced by methods which can be exemplified by—

Di-ethyl Sulphonic Acid, $C_2H_5SO_2.OC_2H_5$, which can be made (*1) by acting with silver sulphite upon ethyl iodide in ethereal solution—

$$2C_2H_5I + AgSO_2.OAg = C_2H_5SO_2.OC_2H_5 + 2AgI$$

In this case, apparently, one of the silver atoms is directly united to the sulphur atom (compare formation of nitro-ethane from $AgNO_2$, p. 110). (*2) It is formed when ethyl sulphonic chloride acts upon sodium ethylate—

$$C_2H_5SO_2Cl + C_2H_5ONa = C_2H_5SO_2.OC_2H_5 + NaCl$$

It is a liquid, b.p. 213°, sp. gr. 1·17.

These neutral esters boil at higher temperatures than the isomeric sulphites. Like them, on boiling with water or dilute alkalis they undergo saponification, but *only one* of the ethyl groups is split off, leaving a sulphonic acid—

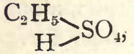
$$C_2H_5SO_2.OC_2H_5 + H_2O = C_2H_5OH + C_2H_5SO_2.OH$$

This shows that in these compounds *one* ethyl group is very differently linked to the other, and supports the conclusions already arrived at as to the constitution of the sulphonic acids.

ESTERS OF SULPHURIC ACID.

Since sulphuric acid is di-basic it can form two series of esters, the acid and neutral salts respectively.

Methyl Hydrogen Sulphate, $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}SO_4$, or *methyl* *sulphuric acid*, is the first example of the acid esters, and is an oily liquid, which does not solidify at −30° C.

Ethyl Hydrogen Sulphate,  $\begin{matrix} C_2H_5 \\ H \end{matrix}\!\!>\!SO_4$, *ethyl sulphuric acid*, *sulpho-vinic acid*, can be formed (*1) by mixing ethyl alcohol with concentrated H_2SO_4—

$$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O$$

The reaction only takes place on heating, and is never complete, but the amount produced increases as the excess of one constituent over another is increased.

Process.—Mix 90 grams of C_2H_5OH and 60 grams of strong H_2SO_4 together; heat to 100° for about an hour, and then allow to stand in a warm place for twenty-four hours. Dilute the mixture with water, and neutralise with either $BaCO_3$ or $PbCO_3$, so as to precipitate the excess of sulphuric acid as $BaSO_4$ or $PbSO_4$. Evaporate the clear liquid to the crystallising point, and decompose the salts of Ba or Pb by H_2SO_4 or H_2S as required. Filter from the precipitate formed, and concentrate *in vacuo* over conc. H_2SO_4.

(2) Ethyl sulphuric acid may also be formed by the combination of ethylene with sulphuric acid.

Properties.—Ethyl sulphuric acid is a colourless, oily liquid, sp. gr. 1·316 at $\frac{16^\circ}{\cdot}$. It has a strongly acid reaction, and does not wet glass. It is soluble in water and alcohol, but not in ether. Its aqueous solution saponifies slowly in the cold, and rapidly when heated, forming alcohol and sulphuric acid—

$$C_2H_5SO_4H + H_2O = C_2H_5OH + H_2SO_4$$

If heated with alcohol to 140°, it yields ether and H_2SO_4—

$$C_2H_5SO_4H + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

Heated alone, it gives first ether, and at a higher temperature ethylene. The remaining basic hydrogen atom may be replaced by metals, with the formation of soluble salts, which decompose on boiling with water or with sulphuric acid.

Methyl Sulphate, $(CH_3)_2SO_4$, is an oil which smells like peppermint, b.p. 188°, and sp. gr. 1·324 at $\frac{16^\circ}{\cdot}$.

Ethyl Sulphate, $(C_2H_5)_2SO_4$, occurs occasionally in the preparation of ether, and may be produced either (1) by the action of SO_3 on alcohol or ether, or (*2) of H_2SO_4 on alcohol; also (3) from ethyl iodide and silver sulphate—

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI$$

It is an oily liquid, b.p. 118° at 40 mm., sp. gr. 1·1837 at $\frac{19^{\circ}}{\cdot}$, and solidifies about $-25°$. It smells like peppermint.

General Remarks on the Esters.

The following methods, which are general in their application to the formation of esters, have received illustration :—

1. Action of acids on alcohols. It should be noted here that these reactions are seldom complete. They are hastened by heat and by the withdrawal from the sphere of action of the water and the ester formed; but, ordinarily, a time arrives at which the saponifying effect of the water formed upon the ester is equal in effect to the esterifying influence of the acid, and a state of equilibrium then ensues.

2. Action of alkyl iodides on silver salts.

3. Action of an alcohol on an acid chloride.

4. Distillation of a salt of the acid of which the ester is required, with an alkyl salt, say of sulphuric acid.

Properties.—All esters (with the exception of nitro compounds and sulphonic acids) can be decomposed by boiling with alkalis, frequently also with water or dilute acids, the alcohol being re-formed; this operation is termed "saponification." The reader must remember that the haloid esters (p. 78) are usually exceptions to this rule, as they yield, except under special circumstances, olefines.

The neutral esters are mostly liquids with an agreeable smell, volatile and neutral in reaction; the acid esters are not volatile without decomposition, and are acid in reaction. The former are almost or quite insoluble in water, the latter readily soluble. Their *constitution* is most readily explained by looking upon them as alkyl salts of the acids from which they are derived; which view is supported by their reactions.

CHAPTER XVI.

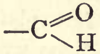
ALDEHYDES AND THEIR DERIVATIVES.

Formaldehyde, CH_2O	Propaldehyde, C_3H_6O
Acetaldehyde, C_2H_4O	Butaldehyde, C_4H_8O, etc.

ALDEHYDES are oxidation products of primary alcohols in which the $—CH_2OH$ group of the alcohols becomes changed to $—CHO$. Probably the first result of such oxidation is to form the group $—CH(OH)_2$. This group, however, is very unstable, and immediately loses water, forming the anhydride or aldehyde, which contains two atoms of hydrogen less than the original alcohol.

This is an illustration of the theory, thoroughly supported by experiment, which holds that, except under exceptional circumstances, no carbon atom can be linked to more than one hydroxyl group. So, *e.g.*, ethyl alcohol, $CH_3.CH_2(OH)$, might be expected to yield, on further oxidation, ethylidene glycol, $CH_3.CH(OH)_2$, while actually it gives acetaldehyde, which is represented by the formula $CH_3.CHO$. While, however, ethylidene glycol is unstable, several of its derivatives are stable, *e.g.* acetal and chloral hydrate, which will be discussed later.

Aldehydes may also be viewed from another standpoint, as reduction products of carboxyl acids, or as hydrides of acid radicles.

As aldehydes are the first oxidation products of alcohols, so acids are the second. It will be remembered that the primary alcohols contain the monad group $—CH_2(OH)$; the aldehydes are characterised as just described by the group $—CHO$ or  $—C\Big\langle^{O}_{H}$; while the carboxyl acids include the group $—CO.OH$. *E.g.* ethyl alcohol is $CH_3.CH_2OH$, acetaldehyde $CH_3.CHO$, and acetic acid $CH_3.COOH$. The group $CH_3.CO$, acetyl, is common to both the aldehyde and the acid, which may therefore be looked upon as the hydride and the hydroxide respectively of that radicle. The fact that aldehydes may be obtained by reducing acids, and also themselves yield the acids by oxidation, supports such view.

It will suffice for our purpose to study the first two members of the series, viz. formaldehyde and acetaldehyde.

Formic Aldehyde or Formaldehyde, H.CHO, *methyl aldehyde.*—This substance probably occurs in plant-cells which contain chlorophyll, and is produced most readily (*1) by the moderated oxidation of the vapour of methyl alcohol—

$$CH_3OH + O = H.CHO + H_2O$$

For this purpose a mixture of the alcohol vapour and air is passed over a heated platinum spiral, or over platinised asbestos, or platinum or copper wire contained in a tube, and the vapour drawn through a condenser. A solution of the aldehyde in methyl alcohol is thus obtained. Loew obtained, by the use of glowing copper, a 15–20 per cent. solution; with a platinum spiral over a spirit-lamp, only 1 per cent. solutions can be obtained.

Process 1.—Fig. 37 shows an apparatus by which small quantities of the aldehyde may be obtained. It consists essentially of a spirit-lamp, in which methyl alcohol is placed. A platinum spiral surrounds the wick. The lamp is ignited, and when the spiral is red hot the flame is extinguished, and the funnel, connected with a condenser and aspirator, is brought down close to the card which is placed on the lamp. With careful adjustment of the amount of air, the wire will continue glowing, and small quantities of the aldehyde can be obtained in a receiver connected with the other end of the condenser.

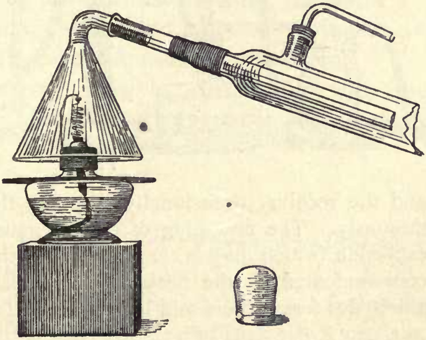


FIG. 37.

†*Process* 2.—For larger quantities, the apparatus shown in Fig.

38 may be conveniently employed. It consists essentially of the flask A, which contains methyl alcohol, and is connected with a hard glass tube 12 inches long, in which are two rolls of copper gauze 2 inches in length at *a* and *b*. The other end of the tube is attached to a spiral condenser, which is connected with a flask that can be cooled by ice water. This is followed by a Woulffe's bottle containing dilute NH_4OH, and the whole is fitted to a filter pump. That part of the hard glass tube containing the gauze *b* is then gently heated, the alcohol warmed to 45–50°, and a current of air, dried by passing through concentrated H_2SO_4, is rapidly drawn through the whole apparatus. If the supply of alcohol is kept up, and the receiver occasionally emptied, the process goes on continuously. The first plug of copper gauze *a* prevents any slight explosion (which may occur on starting the apparatus) from being communicated to the flask. This apparatus will also produce aldehydes from ethers and hydrocarbons.

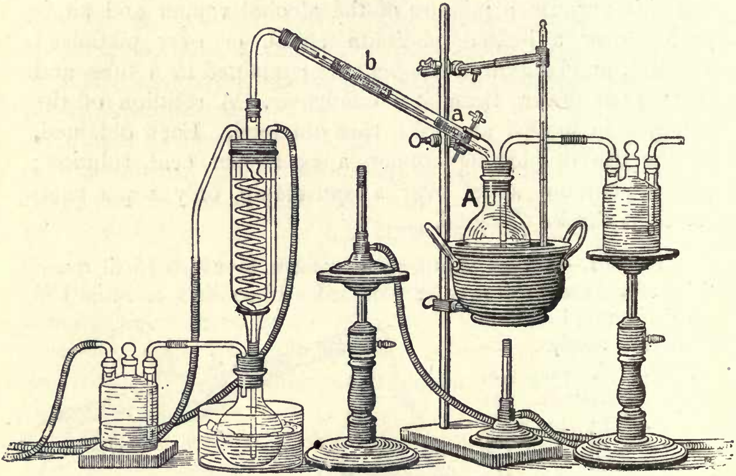


FIG. 38.

Formaldehyde (*2) is also formed when calcium formate is distilled—

$$(H.COO)_2Ca = H.CHO + CaCO_3$$

And (3) by the action of the silent electric discharge on a mixture of CH and CO_2.

Properties.—Formaldehyde is a gas with a very strong pungent odour which excites tears; it is also known in solution; but it is not possible to obtain it pure, because it so very readily polymerises. By freezing the solution usually obtained, and removing the ice formed, it can be concentrated; but if it is evaporated over sulphuric acid or in a vacuum, a white solid, **paraformaldehyde,** is rapidly formed. Warmed for some time with dilute NaOH, formaldehyde yields methyl alcohol and sodium formate.

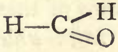
It reacts with ammonia to form **hexamethyleneamine,** $(CH_2)_6N_4$, and if a known amount of ammonia is used, the residual quantity may be determined by titration with sulphuric acid in presence of litmus, and the amount of aldehyde present thus determined. Formaldehyde is a powerful reducing agent; thus with ammoniacal silver solutions, it yields a silver mirror, formic acid being simultaneously formed—

$$H.CHO + Ag_2O = H.COOH + Ag_2$$

It also readily "condenses" in the presence of many bases, producing bodies which apparently belong to the sugars, $(CH_2O)_6$. When formic aldehyde is first treated with H_2S, and then boiled with strong HCl, it yields **tri-thio-methylene,** $(CH_2S)_3$.

Formaldehyde is an antiseptic, and finds employment now as a preservative of milk under the name of "formalin."

Constitution.—It is only possible, consistently with the tetravalency of carbon, to write the formula of formaldehyde thus—



$$H—C\begin{matrix}\diagup H\\ \diagdown\!\!\!= O\end{matrix}\ .$$

The spontaneous formation of **Paraformaldehyde,** $(CH_2O)_3$, has already been noted; and it, and not di-oxy-methane, is also formed when di-iodo-methane (methylene iodide) is treated with silver oxide or heated with silver oxalate. It is a white crystalline body, which sublimes at about 100°, but melts at 153–172°, and *is resolved by heat into the aldehyde.* It is insoluble in cold water, alcohol, and ether, but is soluble in alkalis. When heated to 100° with water, it is resolved into ordinary formic aldehyde; but if a trace of H_2SO_4 is present, and it is heated to about 120°, it is changed into the isomeric α-**tri-oxy-methylene,** which melts at 61°. This body is soluble in water, alcohol, and ether.

Very probably there also exists another polymeride of formic aldehyde that corresponds to the formula $(CH_2O)_2$.

Acetic Aldehyde, or **Acetaldehyde,** $CH_3.CHO$, *ethyl aldehyde.*—This body was given the name aldehyde by Liebig, as a contraction for "alcohol dehydrogenatum," which signified that it was obtained from alcohol by loss of hydrogen.

It occurs in spirit that has been filtered through charcoal, and also in the first runnings of that which is distilled from a Coffey's still (see p. 89), from which it can be obtained by rectification; and is a product of the dry distillation of wood, sugar, and other bodies. Aldehyde is formed (*1) by the oxidation of ethyl alcohol by various oxidising agents, as, for example, air in presence of platinum black; nitric acid, hence its presence in "nitrous ether;" chlorine; chromic acid; and manganic oxide and sulphuric acid—

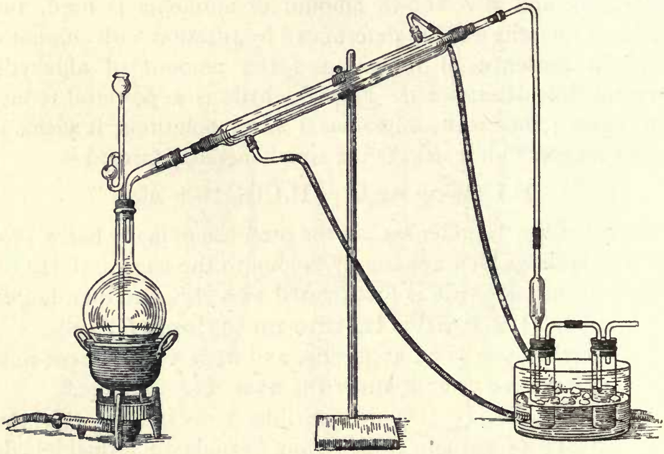


FIG. 39.

$$CH_3.CH_2OH + O = CH_3.CHO + H_2O$$

†*Process.*—Use the apparatus given in Fig. 39. Place in the 1½–2 litre flask 100 grams of granulated $K_2Cr_2O_7$. Add to this a

well-cooled mixture of 400 grams water, 100 grams alcohol, and 140 grams concentrated H_2SO_4. Add the mixture *very gradually*, because heat is evolved and the reaction is often violent. Aldehyde is formed, and distils over through the condenser (the water of which should be kept at about 25°) while most of the alcohol and acetal volatilised at the same time flow back into the flask. The more volatile aldehyde is received in the two cylinders, which are half full of dry ether, and are kept cool by being surrounded with ice and salt. The reaction is completed by applying heat to the flask from the water-bath, and, when over, the tube is disconnected from the condenser and attached to an apparatus which furnishes *dry* ammonia, which is passed into the ether till no further precipitation occurs. Aldehyde ammonia separates as crystals, which can be filtered off, washed with ether, and dried on filter-paper. These crystals, if distilled with H_2SO_4, yield aldehyde, which can then be separated from the aqueous distillate by distillation over fused $CaCl_2$ at a temperature not exceeding 30°.

Aldehyde is also formed (*2) by the dry distillation of a mixture of calcium formate and calcium acetate—

$$(H.COO)_2Ca + (CH_3.COO)_2Ca = 2CH_3.CHO + 2CaCO_3$$

and (*3) it can be obtained by reduction of acetyl chloride or acetic anhydride—

$$CH_3.COCl + H_2 = CH_3.CHO + HCl$$
$$(CH_3.CO)_2O + 2H_2 = 2CH_3.CHO + H_2O$$

Properties.—Aldehyde is a mobile colourless liquid, b.p. 21°, sp. gr. 0·7876 at $\frac{16^\circ}{16^\circ}$. It has a somewhat peculiar ethereal smell, is inflammable, and burns with a blue flame. Its vapour, if inhaled in large quantity, produces cramp of the breast. It is miscible in all proportions with water, alcohol, and ether, and dissolves sulphur, phosphorus, and iodine. If perfectly pure, aldehyde is stable, but very small quantities of other substances render it liable to change.

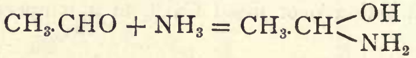
In presence of air it is slowly oxidised to acetic acid; platinum black and other substances increase the speed of change. Acetaldehyde is a strong reducing agent; thus if a little is added to an ammoniacal solution of $AgNO_3$ and gently warmed, a silver mirror is produced—

$$CH_3.CHO + 2AgNO_3 + H_2O = CH_3.COOH + 2HNO_3 + Ag_2$$

the presence of NaOH makes this reaction more sensitive. It also reduces salts of other noble metals, and Fehling's solution. On the other hand, aldehyde is readily reduced by sodium amalgam to alcohol. Aqueous alkalis produce a brown resinous substance when warmed with it.

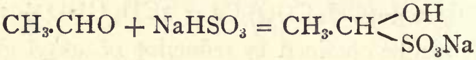
Chlorine acts on it, forming acetyl chloride $CH_3.COCl$; in aqueous solution it forms chloral, $CCl_3.CHO$. When acetaldehyde is treated with PCl_5, ethylidene chloride, $CH_3.CHCl_2$, is produced; similarly PCl_3Br_2 produces the corresponding bromine derivative.

Aldehyde enters into remarkable and characteristic molecular combinations with several reagents; *e.g.* with NH_3, $NaHSO_3$ or $KHSO_3$, and with HCN. With NH_3 it forms aldehyde ammonia (compare formaldehyde)—



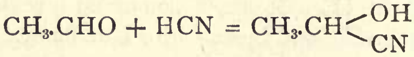
$$\mathrm{CH_3.CHO + NH_3 = CH_3.CH}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}$$

soluble in water and alcohol, insoluble in ether; with a saturated solution of $NaHSO_3$, a crystalline compound—



$$\mathrm{CH_3.CHO + NaHSO_3 = CH_3.CH}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{SO_3Na}\end{matrix}$$

Both this and the aldehyde ammonia are readily decomposed by dilute alkalis or acids yielding the free aldehyde, and can thus be employed for its purification. With HCN it combines, forming ethylidene cyan-hydrin, an oxy-nitrile—



$$\mathrm{CH_3.CHO + HCN = CH_3.CH}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{CN}\end{matrix}$$

this on treatment with dilute HCl yields the corresponding lactic acid (see p. 228). Aldehyde also undergoes characteristic reactions with hydroxylamine and phenyl-hydrazine to form **aldoximes** and **hydrazones** respectively (see these, p. 129).

Constitution of Aldehyde.—It has been said that aldehyde, when treated with PCl_5, yields ethylidene chloride; *i.e.*—

$$CH_3.CHO + PCl_5 = CH_3.CHCl_2 + POCl_3$$

in which *one* atom of oxygen is replaced by *two* atoms of chlorine. Now, it has been already shown (pp. 65, 83) that if oxygen is present as hydroxyl, OH is displaced by Cl, *e.g.*—

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$

i.e. one atom of chlorine for *one* atom of oxygen.

Evidently, therefore, the oxygen is not present as hydroxyl in aldehyde, an inference which is also supported by the non-formation of metallic compounds from it. The oxygen atom is also in all probability linked to one carbon atom only, for, firstly, aldehyde is produced from ethyl alcohol by an analogous reaction to that in which formaldehyde is produced from methyl alcohol, and in that case the oxygen must be linked to one carbon atom; and secondly, that assumption best explains the formation from it by PCl_5, of a di-chlor-ethane which differs from ethylene chloride (see p. 73).

Identification.—The reactions (1) with KOH, and (2) with ammoniacal silver solutions, may be of assistance; (3) if a solution of magenta is decolourised by means of SO_2, and aldehyde added, a deep violet-red shade is obtained. This reaction is given by other aldehydes also. (4) If an alkaline solution of aldehyde is added to a freshly prepared alkaline solution of diazobenzene sulphate, and then a little sodium amalgam is added, a red-violet coloration is produced in about 15 minutes. This is characteristic, and not given by chloral. (5) If a freshly prepared strong aqueous solution of metaphenylene diamine is added to an aqueous or alcoholic solution of aldehyde, a blood-red solution with green fluorescence is formed, which, even if the aldehyde is very dilute (1 : 200,000), shows a yellow rim.

POLYMERISATION AND CONDENSATION OF ALDEHYDE.

Aldehyde readily forms three polymeric modifications, known as **paraldehyde, metaldehyde,** and **aldol** respectively.

Paraldehyde, $C_6H_{12}O_3$, is readily formed by the addition of a few drops of sulphuric acid to aldehyde, when a rise of temperature and contraction of volume occurs. If the liquid is cooled to 0°, the paraldehyde separates. The H_2SO_4 may be replaced by $ZnCl_2$, HCl, or $COCl_2$. Paraldehyde is a colourless liquid, which solidifies to a solid, m.p. 10–12°, b.p.

124°, and sp. gr. 0·999 at $\frac{15°}{15°}$. It is changed back into aldehyde by distilling with H_2SO_4. PCl_5 gives ethylidene chloride.

Metaldehyde, $C_6H_{12}O_3$.—The same reagents which produce paraldehyde will, in a freezing mixture, give metaldehyde; and the best way to prepare it is to pass a few bubbles of HCl or SO_2 into aldehyde surrounded by a freezing mixture, when metaldehyde crystallises out. It forms colourless prisms, which sublime at 115°, and pass into ordinary aldehyde. PCl_5 forms ethylidene chloride.

Neither of these modifications unites with ammonia, alkaline, bisulphites, or hydroxylamine, and they are not affected by hot KOH.

Aldol.—When aldehyde is heated with $ZnCl_2$, or aqueous solutions of sodium acetate or Rochelle salt, *it loses water* and undergoes "condensation," forming **crotonaldehyde**, $CH_3.CH:CH.CHO$. This may really be considered as the result of the second of two reactions, for if aldehyde is allowed to stand for some time with dilute sulphuric acid, a condensation *without* loss of water occurs, with the formation of **aldol**, an alcoholic aldehyde; thus $2CH_3.CHO$ gives $CH_3.CH(OH).CH_2.CHO$, which, when heated with $ZnCl_2$, loses water, and forms the croton-aldehyde just mentioned. This is an example of the aldol condensation of aldehydes.

GENERAL REMARKS ON ALDEHYDES.

The formation of aldehydes from (1) alcohols by oxidation; (2) by distillation of equal molecules of a formate and the salt of the acid corresponding to the aldehyde required; and (3) by the reduction of acid chlorides and anhydrides; have been fully illustrated under formaldehyde and acetaldehyde.

Properties.—The aldehydes are nearly all colourless, volatile liquids; a few are white solids. They possess a characteristic and not unpleasant odour. They are not so readily soluble in water as alcohols, and the solubility decreases with increase of molecular weight. They are all notable for the ease with which they undergo chemical change; their reactions with

NH_3, HCN, $NaHSO_3$, PCl_5, hydroxylamine, and phenylhydrazine, are all characteristic.

Aldoximes.—When aldehydes are suitably treated with hydroxylamine, they produce aldoximes. Thus—

$$CH_3.CHO + NH_2OH = \underset{\text{Acetaldoxime}}{CH_3.CH{:}N.OH} + H_2O$$

It is best to use a solution of hydroxylamine hydrochloride, just neutralised with $NaCO_3$, and then to extract the acidified solution with ether.

The aldoximes are usually liquids which boil without decomposition, and are split up by boiling with HCl into their original components—

$$CH_3.CH{:}N.OH + H_2O = CH_3.CHO + NH_2OH$$

They are reduced by sodium amalgam to the corresponding amines, and form nitriles (p. 193) when acted on by acetyl chloride (see Ketones).

Hydrazones.—A very characteristic reaction is that which the aldehydes enter into with phenyl-hydrazine (an aromatic compound) to form the hydrazones or phenyl-hydrazones; *e.g.*—

$$CH_3\,CHO + C_6H_5.HN.NH_2 = \underset{\text{Acetaldehyde hydrazone}}{CH_3.CH{:}N.NH.C_6H_5} + H_2O$$

The best way to perform this reaction is to make a solution consisting of 1 part phenyl-hydrazine, 1½ parts sodium acetate, and 8 parts water, and add this to the aldehyde in aqueous solution; an oily compound in drops, or a crystalline precipitate is then formed. The hydrazones are not volatile in steam, but are resolved by boiling with dilute HCl into their original constituents.

HALOGEN SUBSTITUTION PRODUCTS OF ALDEHYDE.

Of the chlorine derivatives which may be obtained by the action of chlorine upon aldehyde or alcohol, only one—tri-chloraldehyde, or chloral—merits attention.

Chloral, $CCl_3.CHO$, *tri-chlor-aldehyde.*—(1) This substance, which was discovered by Liebig, is obtained when aldehyde is chlorinated in presence of water and $CaCO_3$, the latter neutralises the HCl liberated; if this precaution is not observed, other products are formed—

$$CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl$$

(2) The ordinary and most convenient method of producing it is by the chlorination of ethyl alcohol.

†*Process.*—Place 100 c.c. of absolute alcohol in a flask, and surround it with cold water, so as to keep the temperature not higher than 10°, then pass in a current of chlorine till the absorption slackens. Next connect the flask with a reflux condenser, warm gently, while still passing in chlorine, till the temperature is 60°, and when no further absorption occurs (shown by there being no further increase of weight), stop the reaction. Finally heat the liquid to the boiling point, then cool down, mix it carefully with an equal volume of strong sulphuric acid, allow to stand, and then distil. Rectify the distillate after standing over $CaCO_3$, and collect the portion which boils between 95° and 100° as chloral.

Manufacture.—The method is identical with the process described. In making large quantities, the first distillation may be omitted, as the chloral separates and may be drawn off.

The reaction involved in the process described is more complex than appears at first sight, and has been shown to occur in the following stages:—

(i.) The alcohol is first oxidised by the chlorine to aldehyde—

$$CH_3.CH_2OH + Cl_2 = CH_3.CHO + 2HCl$$

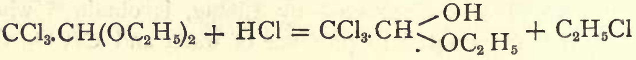
(ii.) The aldehyde formed combines, at the moment of its formation, with alcohol to form **acetal**, the di-ethyl ether of ethylidene glycol (see p. 221).

$$CH_3.CHO + 2C_2H_5OH = CH_3.CH(OC_2H_5)_2 + H_2O$$

(iii.) The acetal in its turn is chlorinated with the production of tri-chlor-acetal—

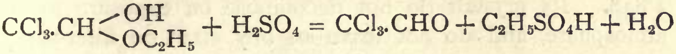
$$CH_3.CH(OC_2H_5)_2 + 3Cl_2 = CCl_3.CH(OC_2H_5)_2 + 3HCl$$

(iv.) The tri-chlor-acetal is acted upon by the HCl produced, leaving "chloral alcoholate," ethyl chloride being simultaneously liberated—



$$CCl_3.CH(OC_2H_5)_2 + HCl = CCl_3.CH\begin{matrix}\diagup OH \\ \diagdown OC_2H_5\end{matrix} + C_2H_5Cl$$

(v.) And finally, on standing with strong sulphuric acid, the alcoholate is decomposed, chloral being liberated—



$$CCl_3.CH\begin{cases}OH\\OC_2H_5\end{cases} + H_2SO_4 = CCl_3.CHO + C_2H_5SO_4H + H_2O$$

Note.—In carrying out the preparation stage (i.) the reaction can be verified by withdrawing a little of the liquid and testing for aldehyde; while the formation of acetal (stage ii.) may be shown later by mixing a little of the liquid with water, when the acetal separates and renders the liquid turbid.

Properties.—Choral is a colourless liquid, with a pungent odour, b.p. 98° (cor.), sp. gr. 1·5292 at $\frac{9^\circ}{9^\circ}$; it has a biting taste, and attacks the skin. It solidifies at -75°, is soluble in water, alcohol, and ether. It is reduced by nascent hydrogen to aldehyde, which body it resembles in combining with NH_3, HCN, and $NaHSO_3$. Chloral reduces ammoniacal silver nitrate solution with formation of a mirror (see Aldehyde); it is oxidised by nitric acid to tri-chlor-acetic acid; and when warmed with NaOH or KOH, *it is immediately resolved into chloroform and a formate*, which can be detected by suitable tests (see Chloroform and Formates).

$$CCl_3.CHO + NaOH = CCl_3H + H.COONa$$

In this decomposition, combined with the reactions given for the formation of chloral from alcohol, we have an explanation *of the chemistry of chloroform manufacture* from alcohol (see p. 74), bearing in mind that in that case calcium hydrate replaces the alkalis. If pure, chloral is quite stable, but small quantities of impurities, especially sulphuric acid, induce polymerisation, with the formation of **meta-chloral.**

When mixed with water, it forms a solid body, termed *chloral hydrate*, which is of considerable technical importance.

Chloral Hydrate, $CCl_3.CH(OH)_2$, *tri-chlor-ethylidene glycol*, is prepared on the large scale from chloral, by mixing it with a suitable quantity of water, and then recrystallising the solid product either from chloroform, or from a mixture of ethylene and ethylidene chlorides which is obtained as a by-product of the chloral manufacture.

Properties.—When pure, chloral hydrate forms colourless transparent monoclinic plates, m.p. 57°, b.p. 97°, and sp. gr. 1·848. Its crystals do not decompose on exposure to the atmosphere, and do not leave an oily stain on filter-paper. It possesses an aromatic odour and a bitter astringent taste. It dissolves readily in water, alcohol, ether, and chloroform. It is decomposed by strong sulphuric acid into chloral and water. It reacts with alkalis in the same manner as chloral, but differs from that substance in not restoring the colour to a solution of magenta which has been decolourised by SO_2.

A very important property of chloral hydrate, discovered by Liebreich in 1869, is that of acting as a powerful hypnotic, and at present large quantities are used in medicine for producing sleep. Whether its action is due to its own specific properties or to the formation of chloroform in the blood, is still a disputed point. The dose given varies from 5–30 grains.

Chloral hydrate for medicinal purposes should answer to the description already given, and should neither give a brown colour if treated with strong H_2SO_4, nor be acid to litmus paper, nor give a precipitate with $AgNO_3$ when in solution in dilute HNO_3.

The following reactions are common to chloral and chloral hydrate: (1) If warmed with alcoholic potash and aniline, the disgusting odour of an iso-nitrile is produced. (2) If boiled with KOH, acidified with acetic acid, and $AgNO_3$ added, silver is precipitated, due to the formic acid formed. (3) The reactions with naphthol and resorcinol, given for chloroform, also serve for these substances, because they yield $CHCl_3$ when decomposed by alkalis.

CHAPTER XVII.

KETONES.

KETONES are readily produced by oxidation of secondary alcohols, and may be considered, like aldehydes, as anhydrides of dihydric alcohols, which are formed by oxidation of the corresponding monohydric compounds. Thus—

$$\underset{\text{Propyl alcohol}}{CH_3.CH_2.CH_2OH} \text{ gives—} \left\{ \begin{array}{l} \text{(i.) } CH_3.CH_2.CH(OH)_2 \\ \text{(ii.) } \underset{\text{Propionic aldehyde}}{CH_3.CH_2.CHO} \end{array} \right.$$

$$\underset{\text{Iso-propyl alcohol}}{CH_3.CHOH.CH_3} \text{ gives—} \left\{ \begin{array}{l} \text{(i.) } CH_3.C(OH)_2.CH_3 \\ \text{(ii.) } \underset{\text{Acetone}}{CH_3.CO.CH_3} \end{array} \right.$$

It is convenient to study them at this point, because they resemble aldehydes in many of their reactions, and the first of the series will be taken as an example.

Acetone, $CH_3.CO.CH_3$, *di-methyl-ketone*, is found in the brain, blood, and urine of diabetic patients. It is produced (1) by the distillation of many organic substances, *e.g.* citric acid and starch, and is obtained in quantity along with wood spirit in the manufacture of pyroligneous acid.

Process.—Acetone may be prepared from crude wood spirit by distilling it from over fused $CaCl_2$, which retains the alcohol. $NaHSO_3$ or $KHSO_3$ is then added in excess to the distillate, and the resulting compound crystallises out. This is pressed, and then decomposed by distilling with dilute Na_2CO_3. The dilute acetone is dehydrated with $CaCl_2$ and rectified.

Acetone may also be formed (*2) by the careful oxidation of iso-propyl alcohol—

$$CH_3.CH(OH).CH_3 + O = CH_3.CO.CH_3 + H_2O$$

(*3) By the dry distillation of acetates of lead, barium, calcium, or other metal (compare Aldehyde)—

$$(CH_3.COO)_2Ba = CH_3.CO.CH_3 + BaCO_3$$

†*Process.*—Distil the barium salt in an iron tube at a moderate

heat. If the salt is pure, then pure dry acetone is obtained. It can be purified, if necessary, by formation of the compound with $NaHSO_3$ as above.

(*4) Its production from zinc methyl and acetyl chloride must be carefully noted—

$$2CH_3.COCl + Zn(CH_3)_2 = 2CH_3.CO.CH_3 + ZnCl_2$$

Properties.—Acetone is a colourless mobile liquid, b.p. 55·6° (cor.), sp. gr. 0·7965 at $\frac{15°}{15°}$. It has a fragrant spirituous odour and a burning taste; it is very inflammable, and burns with a white smokeless flame. It mixes in all proportions with water, and may be separated from its solution by such salts as $CaCl_2$, and K_2CO_3; it is also miscible with both alcohol and ether. Acetone is a useful solvent for many carbon compounds such as fats and resins. It is reduced by hydrogen (sodium amalgam and water) to iso-propyl alcohol, pinacone, $\begin{array}{l}(CH_3)_2C(OH)\\ \quad\;\;| \\ (CH_3)_2C(OH)\end{array}$ also being formed; and, when oxidised with chromic acid mixture, it gives acetic and formic acids—

$$(CH_3)_2CO + 3O = CH_3.COOH + H.COOH$$

The latter acid is broken up in presence of excess of the oxidising mixture into CO_2 and H_2O. *Acetone differs from aldehydes* by not reducing ammoniacal silver nitrate solution. Chlorine and bromine will form substitution products, but in presence of alkalis both those bodies and iodine react to form chloroform, bromoform, and iodoform (see pp. 74–76).

$$C_3H_6O + 6Cl_2 + H_2O = 2CHCl_3 + CO_2 + 6HCl$$

PCl_5 forms di-chlor-propane, $CH_3.CCl_2.CH_3$. *Similarly to aldehyde*, acetone combines with $NaHSO_3$ to form the compound, $(CH_3)_2C{<}\begin{array}{l}OH\\SO_3Na\end{array}$, which is decomposed by dilute alkalis; and with HCN to form a cyanhydrin, $(CH_3)_2C{<}\begin{array}{l}OH\\CN\end{array}$.

With hydroxylamine it forms an **oxime, acetoxime,** $(CH_3)_2C{:}N.OH$, and with phenyl-hydrazine it yields **acetone-hydrazone,** $(CH_3)_2C{:}N.NHC_6H_5$.

Its reaction with NH_3 is also complicated, a body called **acetonamine** being formed with elimination of water—

$$2(CH_3)_2CO + NH_3 = CH_3.CO.CH_2.C(CH_3)_2NH_2 + H_2O$$

Constitution.—The constitution hitherto assigned to acetone is supported by the following considerations: (1) It can be shown by the action of PCl_5 to contain the carbonyl group CO, this conclusion being supported by its formation by oxidation of a secondary alcohol, and general likeness to aldehyde; and (2) its synthesis from zinc methyl and acetyl chloride leads to the same formula.

Identification.—(1) The following is a delicate reaction for the detection of acetone: Add excess of NH_4HO to the solution; then iodine in a solution of NH_4I, till the black precipitate of NI_3 first formed only disappears slowly, and in presence of acetone the solution becomes milky, and iodoform separates; *by this method acetone can be detected in presence of ethyl alcohol.* (2) If a solution of $HgCl_2$, made strongly alkaline with alcoholic KOH, is added to a solution containing acetone, and the whole shaken, a part of the mercuric oxide is dissolved, and, after filtration, may be detected in the filtrate, either by adding Am_2S or by acidifying with HCl and adding $SnCl_2$. (3) Add to an aqueous solution of acetone a little sodium nitro-prusside, then some very strong NaOH solution; a bright red colour is produced, which goes yellow on standing; acetic acid turns it to a bluer red.

GENERAL REMARKS ON KETONES.

The formation of acetone illustrates the general formation of ketones (1) by oxidation of secondary alcohols; (2) by distillation of salts of fatty acids; and (3) from acid chlorides and zinc alkyls. The last two methods can, of course, be modified so as to form *mixed* as well as simple ketones—

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium propionate}}{(C_2H_5COO)_2Ca} = \underset{\text{Methyl-ethyl ketone}}{2CH_3.CO.C_2H_5} + 2CaCO_3$$

Besides the above synthetical methods, they frequently result from the destructive distillation of organic substances.

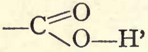
Properties.—The ketones are either colourless, aromatic-smelling liquids, which boil without decomposition, or, beginning with $C_{13}H_{26}O$, crystalline solids. Aldehydes, which contain the same number of carbon atoms, are isomeric with them. Some of the ketones are easily soluble in water, others only a little or not at all, but they mix in all proportions with alcohol and ether.

Many of their reactions and combinations are similar to those of the aldehydes; thus ketones which contain the group $CH_3.CO$ unite with the acid sulphites of the alkalis to form compounds which are decomposed by dilute alkalis; the others, however, do not, with the exception of propione, $(C_2H_5)_2CO$, which does so with difficulty. The reactions of acetone with NH_3, HCN, hydroxylamine and phenyl-hydrazine, with reducing and oxidising agents, and with Cl, Br, or PCl_5, are quite typical of the series. They may be distinguished from isomeric aldehydes by not reducing ammoniacal silver solutions.

Note.—The student will do well to tabulate for himself the similarities and differences of the aldehydes and ketones in regard to their preparation; and of their reactions, more especially with reducing and oxidising agents, hydroxylamine, phenyl-hydrazine, alkaline sulphites, PCl_5, etc.

CHAPTER XVIII.

SATURATED MONOBASIC ACIDS OF THE ACETIC SERIES, OR FATTY ACIDS, $C_nH_{2n}O_2$.

It has been already stated (p. 120) that the carboxyl acids are the second oxidation products of alcohols, and contain the atomic group, —CO.OH, or  $-C\begin{smallmatrix}\nearrow O \\ \searrow O-H\end{smallmatrix}$, which is therefore characteristic of them.

The principal acids of the series are the following:—

Formic acid,	H.COOH	Valeric acids,	C_4H_9COOH
Acetic ,,	$CH_3.COOH$	Caproic ,,	$C_5H_{11}COOH$
Propionic ,,	$C_2H_5.COOH$	Palmitic ,,	$C_{15}H_{31}COOH$
Butyric acids,	$C_3H_7.COOH$	Stearic acid,	$C_{17}H_{35}COOH$

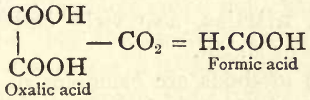
Only a few of these acids will be considered in detail.

Formic Acid, $H.COOH$, *hydrogen-carboxyl acid.*—Formic acid was first obtained by distilling red ants (*Formica rufa*); hence its name. It is present in various animal fluids, as, *e.g.*, in human blood, sweat, urine, and in the muscles, and in certain caterpillars. It is also found in plant-juices, as in the common stinging-nettle, in tamarinds, and in various pines; and certain mineral springs contain its salts.

(1) Formic acid was early prepared by distilling starch with H_2SO_4 and MnO_2; many other substances, such as sugar, gums, and grain, yield it when similarly treated. (*2) It is also produced when methyl alcohol is oxidised, *e.g.* by means of air in presence of platinum black.

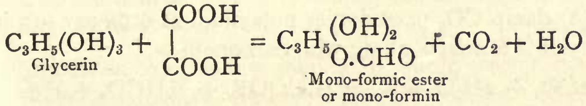
Experiment 15.—Place a small portion of platinum black on a watch-glass, moisten with the alcohol, press a piece of blue litmus paper into the mixture, and then cover with a beaker. Reddening of the litmus paper shows the presence of the acid.

(3) Formic acid is produced most conveniently in quantity by heating oxalic acid, either alone or better with glycerin, when it loses CO_2 and leaves formic acid—



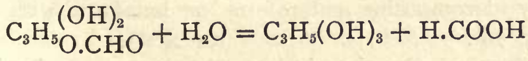
$$\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}} - CO_2 = \underset{\text{Formic acid}}{H.COOH}$$

Really, however, in presence of glycerin the reaction occurs in three stages: (i.) The crystallised oxalic acid, when heated, loses its water of crystallisation, and is (ii.) decomposed by glycerin, thus—



$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + \begin{array}{c}COOH\\|\\COOH\end{array} = \underset{\substack{\text{Mono-formic ester}\\\text{or mono-formin}}}{C_3H_5\begin{array}{l}(OH)_2\\O.CHO\end{array}} + CO_2 + H_2O$$

(iii.) On further addition of crystallised oxalic acid, that substance at once forms the anhydrous acid and water; which latter converts the ester into glycerin and formic acid—



$$C_3H_5\begin{array}{l}(OH)_2\\O.CHO\end{array} + H_2O = C_3H_5(OH)_3 + H.COOH$$

and the reaction between the oxalic acid and the glycerin once more occurs.

†*Process.*—Attach a ½-litre distilling flask to a Liebig's condenser and receiver. Introduce into it 200 c.c. of concentrated glycerin and 50 grams of crystallised oxalic acid. Heat the mixture on an oil-bath to about 108–110°. A brisk evolution of CO_2 occurs, and dilute formic acid distils over. When the reaction is complete, repeat the addition of 50 grams oxalic acid and subsequent distillation three times. (The addition of oxalic acid may be repeated an *indefinite number* of times.) The distillate contains about 50 per cent. of acid; boil it with lead carbonate so as to form lead formate. Filter and concentrate to the crystallising point, when crystals of lead formate are obtained. From these the free acid may be prepared if desired by passing dry H_2S over them in a tube heated to 100°, and rectifying it afterwards over more of the salt to free it from sulphur compounds.

Another method of great interest is (*4) the formation of formic acid from hydrocyanic acid, HCN, in presence of dilute acids or alkalis—

$$\mathrm{HCN + 2H_2O + HCl = H.COOH + NH_4Cl}$$

This reaction is the first instance of a valuable general method of producing acids; for alkyl salts of hydrocyanic acid, or, as they are termed, **nitriles**, also yield carboxyl acids when treated with acids or alkalis.

The next two methods are examples of syntheses of the acid from its elements, for (5) when carbon monoxide is passed over moist KOH at 100–200° C., or over moist soda-lime at 200°, formates are produced—

$$\mathrm{KOH + CO = H.COOK}$$

and (6) damp CO_2 passed over potassium at ordinary temperatures yields formates along with carbonate—

$$\mathrm{2CO_2 + 2H_2O + K_2 = H.COOK + KHCO_3 + H_2O}$$

Besides these methods, formic acid is produced by the reduction of ammonium carbonate, by the action of the silent electric discharge on a mixture of carbon dioxide and hydrogen, and by decomposing chloroform or iodoform with alkalis (pp. 75, 76).

Properties.—Formic acid is a colourless mobile liquid, b.p. 100°, sp. gr. 1·245 at $\frac{0°}{4°}$, which freezes to a solid, m.p. 8·6°.

It has a pungent smell, a sour taste, and acts very violently on the skin, producing blisters, and ultimately painful wounds. Addition of water first lowers the boiling point and then raises it, a mixture of 77 parts of acid and 23 parts of water boiling at 107°, being always obtained on repeated distillation of the acid. It is a stronger acid than acetic acid, and is a more powerful antiseptic than phenol. Formic acid is readily decomposed by concentrated H_2SO_4, with formation of carbon monoxide—

$$H.COOH = H_2O + CO$$

It is a powerful reducing agent, its salts reducing alkaline solutions of gold and platinum salts, with separation of the metal; reducing Fehling's solution with precipitation of Cu_2O; and the free acid reduces silver nitrate solution when warmed, with separation of silver and formation of CO_2—

$$H.COOH + Ag_2O = Ag_2 + CO_2 + H_2O$$

Formates do *not* reduce ammoniacal silver nitrate. The acid reduces permanganate of potash and chromic acid. Neutral solutions of formates give a red colour with $FeCl_3$.

It is probable that the powerful reducing properties of formic acid are due to the fact that, although an acid, it also contains the aldehydic group H.CO, thus differing from the higher members of the series.

Constitution (see p. 145).

Identification.—The reactions with $AgNO_3$, Fehling's solution, $FeCl_3$, and chromic acid serve to identify and to distinguish formic acid from acetic acid.

Formates are readily soluble in water, except the lead and silver salts, which are only sparingly soluble. The salts of the alkali metals yield the corresponding oxalates when carefully heated to 250°.

Acetic Acid, $CH_3.COOH$, *pyroligneous acid*, has been known, in the dilute and crude form as vinegar, from very ancient times. It is found both in the free and in the combined states in some animal, and many plant juices. It exists, for example, in some plants as the calcium, in others as the potassium salt; and esters of it, with glycerin and other alcohols, occur in many oils and fats.

Apart from methods which are of purely scientific interest, there are two processes by which acetic acid is produced in a more or less pure state, which from their industrial importance specially claim attention.

(1) Acetic acid is a product of the oxidation of ethyl alcohol by means of air in presence of platinum sponge, chromic acid, certain ferments, and other substances, the reaction occurring in two stages, *i.e.* of alcohol to aldehyde and from that to acid—

$$\text{(i.)}\ CH_3.CH_2OH + O = CH_3.CHO + H_2O$$
$$\text{(ii.)}\ CH_3.CHO + O = CH_3.COOH$$

Process.—Its formation by this method may be demonstrated as follows: Place a small quantity of alcohol in a dish, over that put a tray containing platinum sponge, and cover the whole with a bell jar which is open at the top and raised from the table at the bottom. Now gently warm the alcohol; acetic acid will be rapidly formed and condense on the sides of the jar. Its presence may be detected by its odour and its action on blue litmus paper.

This method has actually been used for producing the acid in quantity, but its cost has prevented its general adoption.

Crude acetic acid is, however, made from alcohol by the oxidising action of a microscopical organism, the *Bacterium* or *Mycoderma aceti* (Fig. 40), which grows upon the surface of the liquid. Pure alcohol remains entirely unaffected if exposed to the action of the ferment; if, however, weak alcohol is mixed with alkaline earthy and ammonium phosphates, these supply the nutriment necessary for the growth of the organism, and acetic acid is then produced. In the manufacture of vinegar, the salts which the plant requires are found in the extract from the various fruits and grain, and the albuminous matter which is present furnishes the nitrogen.

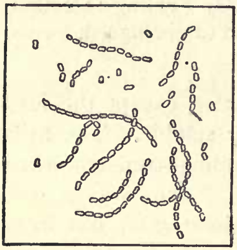


FIG. 40.

In order to produce vinegar from fermented liquors by the acetous fermentation, the amount of alcohol present must not be too great, or the oxidation will not take place; *e.g.* in France, in the manufacture of wine vinegar, it is customary to work as far as possible with a wine which contains about 10 per cent. of alcohol. On the other hand, if only 3 per cent. is present, it acetifies too slowly.

Manufacture.—*Wine vinegar* is made in 50–100 gallon casks, provided with holes for charging and allowing circulation of air, and arranged in buildings termed "vinageries." They are first filled one-third full of boiling vinegar , after a week a small charge of wine is added, and this is repeated every week till the cask is two-thirds full, when part of the vinegar is drawn off, and the charging commences afresh. The temperature is kept about 25–27° during the process.

Quick Vinegar Process.—To increase the speed of production, Schutzenberger devised an apparatus, the "Graduator" (Fig. 41), which consists of a large oak tun, A. At a convenient distance from its bottom a number of holes, *a*, about 1 inch in diameter are bored, and a perforated false bottom, *b*, is placed just above these. Deal shavings are piled on this nearly to the level of the top, *c*, which has its perforations loosely packed with cotton wick, and contains, besides the small holes thus partially closed, several larger ones, in which glass tubes are fixed. The whole is then covered with a well-fitting lid with a hole in the top.

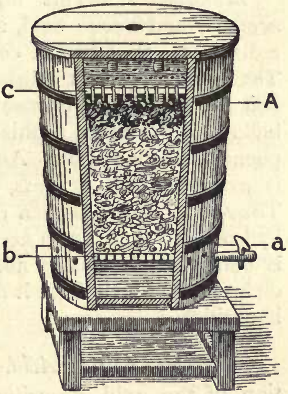


FIG. 41.

To start the apparatus, vinegar heated to about 25° is poured in, and it drips down by means of the cotton and spreads over the whole surface of the shavings. In a day or two, weak spirituous liquor is poured in and descends similarly. The shavings become covered with the *Mycoderma aceti*, and expose a large surface to the liquor, while a current of air also passes up through the cask. The vinegar formed can be periodically withdrawn by means of the bent tube and tap.

It is possible, by the use of this apparatus, to prepare very strong vinegar if the liquor is passed through more than one graduator, as only about 4 per cent. of alcohol is transformed at one passage. It is necessary to carefully regulate the speed of working and the temperature, or else loss of alcohol occurs.

Malt vinegar is made from fermented wort by processes which are identical in principle, though differing in detail, from those just mentioned.

The vinegars obtained differ in their properties. They may be colourless from white wines or spirits, or brown from malt; in some cases they are coloured artificially. The amount of acid varies from 4 to 15 per cent. in different vinegars. The B.P. malt vinegar should contain 6 per cent. acid, and have a sp. gr. of 1·019.

(2) Acetic acid is also made in quantity from the acid tarry liquid obtained when wood is distilled in closed vessels.

Manufacture.—This liquid contains principally wood spirit, acetone, and acetic acid, and, after separation from the tar, is redistilled. Wood spirit comes over first, and then a crude acid. The impure liquid is neutralised with lime, then allowed to settle, and the clear liquid is drawn off and evaporated down to half its bulk. HCl is added to this till it is *just acid;* this causes tar and phenols to separate out. After separation the clear liquid obtained is evaporated to dryness, and heated to char any impurities. The solid residue is then distilled with the necessary quantity of hydrochloric acid, when acetic acid of about 50 per cent. strength is obtained. If this is not pure, it is distilled with potassium dichromate, which frees it from traces of HCl and empyreumatic impurities.

Glacial Acetic Acid.—By repeated fractional distillation of the acid described, and separation of the higher-boiling portion, an acid is obtained which solidifies on cooling; this is termed glacial acetic acid.

It is, however, usually produced by forming the sodium salt, carefully and completely drying this, and then distilling it with strong H_2SO_4. The acid so obtained must be distilled at least once more, as it contains a little water from the sulphuric acid. A dilute acid distils over first, and then the anhydrous acid; this crystallises on cooling, and the crystals, separated, drained, and redistilled, yield a pure acid.

The methods of production of acetic acid hitherto considered have been of technical importance; there are others which must be mentioned, because of their scientific interest.

Thus (*3) aceto-nitrile (methyl cyanide), when boiled with acids or alkalis, yields either the acid or its salt—

$$CH_3.CN + NaOH + H_2O = CH_3.COONa + NH_3$$

While (*4) when carbon dioxide acts upon sodium methyl, sodium acetate is produced—

$$CH_3Na + CO_2 = CH_3.COONa$$

Also (*5) if sodium methylate is heated to 160° with carbon monoxide, the sodium salt is formed—

$$CH_3ONa + CO = CH_3.COONa$$

Compare the last three reactions with reactions 4, 5, and 6, employed for preparing formic acid (p. 138).

The student should specially notice the means by which the synthesis of acetic acid from its elements is possible. The synthesis of alcohol by successive formation of acetylene, ethylene, and ethyl hydrogen sulphate has been given on p. 85, and since alcohol on oxidation yields the acid, the synthesis of the latter body is also possible. But acetylene can also be oxidised directly in presence of dilute potash, with the formation of potassium acetate—

$$C_2H_2 + KOH + O = CH_3.COOK$$

which furnishes another means of synthetically forming acetic acid.

Properties.—Pure anhydrous acetic acid is a transparent mobile liquid, b.p. 118·3°, sp. gr. 1·0543 at $\frac{16^\circ}{4^\circ}$. At about 17° it freezes to a crystalline solid, m.p. 16·5°. The acid has a pungent odour and a sour taste. It attacks the skin, producing blisters, and its vapour burns with a pale blue flame. If *quite anhydrous* it has *no action upon litmus paper*, although it reddens it in aqueous solution. It dissolves in water in all proportions, but the specific gravity of the acid does not vary in proportion to its strength; in fact, a solution containing only 33 per cent. of acid has the same specific gravity at 15° as anhydrous acid. Acetic acid is not readily acted upon by sulphuric or nitric acids. Chlorine attacks it, forming chlor-substitution products; PCl_5 and PCl_3 form acetyl chloride (*q.v.*); and it can be reduced successively to acetaldehyde and alcohol. It is a useful solvent for many organic bodies, and finds considerable employment in the arts in the preparation of the various acetates, etc.

Identification.—(i.) $FeCl_3$ solution gives, with a solution of the acid made neutral with NaOH or KOH, a red coloration, and the liquid yields a flocculent brown precipitate when boiled. (ii.) Dry potassium acetate gives, when heated with a *small* quantity of As_2O_3, the disgusting odour of cacodyl (poisonous). (iii.) Add a small quantity of ethyl alcohol to a solution of the acid or a salt, and then an equal volume of strong sulphuric acid, and warm gently; the odour of ethyl acetate is produced. (iv.) If in the last test the ethyl alcohol is replaced by amyl alcohol, the fragrant smell of jargonelle pears (due to amyl acetate) is obtained.

SALTS OF ACETIC ACID.

Most of the acetates are readily soluble in water, the silver and mercury salts dissolving with least readiness. As a rule they are also soluble in alcohol (*distinction from formates*). Some, such as the iron and aluminium salts, decompose, on boiling their solutions, into basic acetates, which are precipitated, and free acetic acid. All acetates are decomposed by heat, acetone being usually formed in greater or less quantity. Among the principal salts are the following:—

Aluminium Acetate, $Al(C_2H_3O_2)_3$ or $\overline{Al}A_3$, is not known in the solid form, since it decomposes on evaporation; but in solution in an impure form, which is usually prepared by decomposing lead acetate with aluminium sulphate, it finds very considerable use, under the name of "red liquor," as a mordant in calico-printing. It decomposes on heating, losing acetic acid and leaving a basic salt.

Copper Acetates.—Of these, the normal cupric acetate,

$Cu\bar{A}_2.H_2O$, forms dark green efflorescent crystals; but more important is *verdigris*, which is a mixture of basic acetates of copper, and is prepared by exposing copper to the fumes of acetic acid, as, for example, those arising from fermenting wine lees. It is a green solid, which finds some use as a mordant in dyeing silk black. It is also used in the manufacture of paints.

Iron Acetates.—Of these the crude ferrous acetate, known as *pyrolignite of iron*, *black liquor*, or *iron liquor*, is technically of great importance. It is a deep black liquor, with a strong and characteristic smell, prepared by dissolving scrap-iron in pyroligneous acid, hence its odour; and its dark colour is due to a compound of triferric tetroxide formed on exposure to air. It is used in mordanting and preparing both cotton and silk for black dyeing, and for other colours.

Lead Acetates.—Normal lead acetate, $Pb\bar{A}_2.3H_2O$, *sugar of lead*, is produced when the oxide or carbonate is dissolved in acetic acid. If crude acid is employed, *brown acetate* is formed. When pure it forms white crystals, which readily effloresce, and are easily soluble in water and ordinary alcohol, but insoluble in absolute alcohol. It is sometimes employed in dyeing. There are several basic acetates; one of these, which may be prepared by dissolving litharge in a solution of the acetate, is employed in pharmacy in dilute solution as *Goulard water*.

CONSTITUTION OF ACETIC AND FORMIC ACIDS.

So far it has been assumed that the constitution of acetic acid is represented by the formula $CH_3.COOH$; but it is necessary now to inquire upon what data that formula rests. The elementary analysis of acetic acid gives numbers which lead to the empirical formula, CH_2O; if, however, the silver salt is analysed, numbers are obtained which yield the formula $C_2H_3O_2Ag$, which corresponds to that of $C_2H_4O_2$ for the acid itself, or twice the former number. This latter formula is proved, by a determination of the vapour density, to be also the molecular formula.

These results, however, tell us little about the constitution; the only light they throw on that is this, that in the formula $C_2H_4O_2$ there is one hydrogen atom, which is replaceable by metals, so that the formula might be written $C_2H_3O_2H$ in order to indicate this.

It will be remembered that in studying alcohols we found that the (OH) group was replaceable by halogens, if suitable reagents were employed (see p. 65). If now acetic acid is treated with PCl_5, a substance which is called acetyl chloride is obtained (the group C_2H_3O' being termed acetyl), and corresponds to the formula C_2H_3OCl. This substance reacts with water, the acid being re-formed and the chlorine eliminated as hydrochloric acid; this reaction, therefore, proves the presence of an OH group in the molecule, so that the formula can now be written $C_2H_3O.OH$.

But further, when acetyl chloride is treated with nascent hydrogen, the chlorine atom is displaced by hydrogen, and aldehyde is formed, $C_2H_3.O.H$. This, however, has been shown (p. 127) to contain oxygen bound directly to carbon by both bonds, since when PCl_5 acts on it the compound $C_2H_4Cl_2$ is obtained. We can therefore now write the formula for acetic acid $C_2H_3.O.OH$.

The next thing to determine is whether the OH and the O are united to *the same* or *different* carbon atoms, and numerous reactions lead to the conclusion that they are bound to the same carbon atom. Thus (i.) the saponification of methyl cyanide (prepared by acting on methyl iodide with KCN, *i.e.* CH_3I, yields $CH_3.CN$), which, on boiling with dilute acids (p. 143), yields the corresponding acid, with elimination of the nitrogen as ammonia—

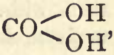
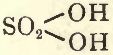
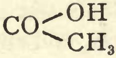
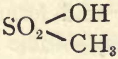
$$CH_3.CN + 2H_2O + HCl = CH_3.COOH + NH_4Cl$$

and (ii.) the synthesis of an acetate from sodium methylate and carbon monoxide, and from sodium methide and carbon dioxide (p. 143), as well as the fact that acetic acid on electrolysis yields ethane (see p. 44), all go to show that the methyl group exists as such in acetic acid, so that the formula can be written in the extended form, $CH_3.CO.OH$, which has been shown, therefore, to rest on a sound experimental basis.

With regard to the constitution of formic acid, CH_2O_2, that follows from similar considerations to those just mentioned; so, for example, it is formed by the oxidation of methyl alcohol; by the saponification of HCN analogously to that of $CH_3.CN$; and its syntheses from CO and KHO, and CO_2 and H_2, are not readily explicable by any other formula than H.CO.OH.

Acetic acid may therefore be looked upon as derived from formic acid by the replacement of a hydrogen atom by CH_3, and all other mono-basic acids may be similarly derived.

Thus all alcohols are derivable from $H.CH_2OH$
,, aldehydes ,, ,, H.COH
and ,, acids ,, ,, H.COOH

From another standpoint carboxylic acids can be looked upon as related to the hypothetical carbonic acid,  $CO{<}^{OH}_{OH}$, by the replacement of one OH group by an alkyl radicle, while sulphonic acids are similarly derivable from sulphuric acid,  $SO_2{<}^{OH}_{OH}$; *e.g.*  $CO{<}^{OH}_{CH_3}$ and  $SO_2{<}^{OH}_{CH_3}$

HALOID SUBSTITUTION PRODUCTS OF ACETIC ACID.

Acetic acid yields haloid derivatives when treated with chlorine or bromine, in which the hydrogen of the methyl group is replaced by the halogen element; from these the iodo-derivatives can be prepared, as well as numerous other compounds.

Mono-chlor-acetic Acid, $CH_2Cl.COOH$, is prepared by the chlorination of acetic acid.

†*Process.*—Pass chlorine into gently boiling glacial acetic acid in a flask provided with a reflux condenser; if performed in sunlight, the operation is complete in about fifteen hours, without sunlight it takes at least thirty hours. Distil the product with the thermometer *in* the liquid, and collect apart that which distils between 130° and 190°. By repeated rectification of this distillate

a liquid boiling between 185° and 187° is obtained; allow this to crystallise, press the crystals, and dry *in vacuo* over H_2SO_4 and solid KOH. The crystals will then distil at about 186°.

Properties.—Chloracetic acid crystallises in needles or prisms, m.p. 63°, b.p. 186°; is strongly acid, and soluble in water. The chlorine in it is replaceable by a number of radicles, *e.g.* OH, NH_2, CN, and SO_3H, by similar processes to those employed in preparing similar derivatives of the hydrocarbons, with the formation of hydroxy-acetic, amido-acetic, cyan-acetic, and sulpho-acetic acid respectively.

Trichlor-acetic Acid, $CCl_3.COOH$, is prepared by the oxidation of chloral with concentrated HNO_3, as—

$$CCl_3.CHO + HNO_3 = CCl_3.COOH + HNO_2$$

†*Process.*—Heat 100 grams of chloral hydrate till it is just melted, in a 300–400 c.c. flask with a round bottom, and add carefully 40 grams of fuming HNO_3. Heat till the reaction commences, then withdraw the flame. When no more nitrous fumes are evolved, and the reaction is over, distil the product; that which comes over between 193° and 196° is nearly pure tri-chlor-acetic acid.

Tri-chlor-acetic acid forms deliquescent scales, m.p. 55°, b.p. 195°. It is very soluble in water, and strongly acid.

CHAPTER XIX.

FATTY ACIDS—Continued. GENERAL METHODS—HIGHER MEMBERS.

General Remarks on Fatty Acids.

Having now discussed the preparation and properties of formic and acetic acids, we are in a position to speak of the acids more generally.

The following methods of formation, which are of general use, have already been illustrated by the before-mentioned acids; thus acids are formed—

1. By the oxidation of alcohols and aldehydes.

2. By the saponification of alkyl cyanides (nitriles) by heating with alkalis, dilute acids, or water.

3. By the action of CO upon sodium alcoholates at high temperatures.

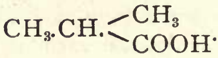
4. By the action of CO_2 upon sodium alkyls.

Besides these methods, they may be formed—

5. By the action of strong KOH on aceto-acetic esters (see p. 283); (6) by the dry distillation of di-basic acids of the Malonic series (see p. 240); and (7) frequently by the decomposition of their naturally occurring esters, the fats and oils.

Properties.—With the exception of the first three acids, the lower members of the series are oily liquids; from capric acid upwards they are solids. The liquids have a strongly acid, sometimes disagreeable, odour; the solids are without smell. The lower members are soluble in water; as the molecular weight increases their solubility decreases, till from C_{10} they are insoluble. All are easily soluble in alcohol and ether. The lower acids are readily volatilised, but those of high molecular weight are not volatile without decomposition, except at greatly diminished pressures. They can, however, all be easily distilled in a current of steam.

The boiling point of acids of like structure increases about 19° for every increment of CH_2; but though the melting point of the acids also increases with increase of molecular weight, acids containing an *even* number of carbon atoms always possess a higher melting points than those with an uneven number of carbon atoms next following them in the series. The fatty acids do not redden litmus paper *per se*, but do so in solution. They form salts with bases, and chlorine and bromine act upon them, forming substitution derivatives. Amongst their characteristic reactions must be remembered (1) that they can be reduced to aldehydes and then to alcohols; (2) that their lime salts, on dry distillation, yield ketones (if a mixture of the salts of two acids is employed *mixed* ketones result, unless one salt is a formate, when aldehydes are produced); (3) if the dry sodium salts are distilled with soda lime or sodium methylate, they lose CO_2, and hydrocarbons are produced; (4) on electrolysis they lose CO_2 with the formation of hydrocarbons; and (5) that PCl_5 acts upon them, displacing OH and forming acid chlorides.

Isomerism in the Acids.—Isomerism in these acids depends upon the same causes as those mentioned in speaking of the halogen derivatives of propane, and of the alcohols (p. 79). For since they are mono-derivatives of hydrocarbons, the number of isomers that can be formed depends upon the number of different positions which the carboxyl group, COOH, can take in the hydrocarbon molecule. Thus there can only be *one* propionic acid, $CH_3.CH_2.COOH$, since it may be looked upon as ethane in which hydrogen is replaced by carboxyl; on the other hand, propane can yield *two* derivatives according to the carbon atom to which the carboxyl group is attached, and consequently there can be two butyric acids, viz. butyric acid, $CH_3.CH_2.CH_2.COOH$, and iso-butyric acid,  $CH_3.CH.\begin{matrix}\diagup CH_3 \\ \diagdown COOH\end{matrix}$.

Propionic Acid, $CH_3.CH_2.COOH$, may be prepared by several of the general methods, *e.g.* from propyl alcohol, from propionitrile, from sodium ethylate, as well as by the fermentation of calcium malate and lactate.

Properties.—It is a colourless, somewhat oily liquid, with a smell that resembles both acetic and butyric acids; b.p. 140°, sp. gr. 1·016 at 0°. It is soluble in water, but $CaCl_2$ throws it out of solution. Its salts are all soluble in water, and generally crystallise readily.

Butyric Acids.—Two isomers.

n-Butyric Acid, $CH_3.CH_2.CH_2.COOH$, occurs either free or combined in many natural products. It is present, combined with glycerin, in butter, and occurs free in rancid butter. It is also found in cod-liver oil, in muscular juice, and in perspiration, and its esters are found in several fruits. It may be formed from butyl alcohol, and from propyl cyanide, is a product of the fermentation of calcium lactate, and also of many vegetable and animal substances by a species of schizomycetes. It has been shown, for example, that *Bacillus subtilis* acts upon starch, producing butyric acid.

Process.—Butyric acid is prepared by the fermentation of sugar, thus: dissolve 6 kilos. of sugar and 30 grams of tartaric acid in 26 litres of hot water, and allow to stand some days; then add 250 grams of putrid cheese, 8 kilos. of sour skimmed milk, and 3 kilos. of chalk. Keep the mixture at 30–35°, stirring every day. At the end of a week a thick magma of calcium lactate is formed, which on longer standing liquefies once more, CO_2 and H being evolved. The reaction is over at the end of six weeks, and calcium butyrate remains in solution. Then precipitate the calcium by adding 8 kilos. Na_2CO_3, 10 H_2O, and decompose the sodium salt formed by adding 11 kilos. dilute H_2SO_4. The crude acid which separates may be purified by forming its ethyl ester, rectifying that (b.p. 121°), and then saponifying it.

The formation of butyric acid occurs in several stages.

Sugar, $C_{12}H_{22}O_{11}$, first forms glucose, $C_6H_{12}O_6$, by absorption of water, that yields lactic acid, $C_3H_6O_3$, which then forms butyric acid according to the equation following—

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$$

Properties.—It is a strongly acid liquid, with a disagreeable rancid odour, b.p. 162° (cor.), sp. gr. 0·967 at $\frac{15^\circ}{15^\circ}$, and on cooling solidifies to a white mass, which melts at about -3°. It is a strong acid, which attacks the skin, is miscible with water in all proportions, and thrown out of solution by salts, *e.g.* $CaCl_2$.

Its salts are soluble in water; the calcium salt is less soluble in hot than in cold water, and on heating for some time to 100° it forms calcium iso-butyrate.

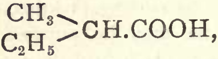
Iso-butyric Acid, $(CH_3)_2CH.COOH$, is found in carobs (St. John's bread), in *Arnica montana*, in Roman oil of chamomile, and in croton oil. It is formed, by general methods, from iso-propyl cyanide; and from iso-butyl alcohol.

Properties.—Iso-butyric acid is a liquid, very similar in smell to the normal acid, but not so unpleasant; b.p. 153° (cor.), sp. gr. 0·9539 at $\frac{15^\circ}{15^\circ}$. It differs from the normal acid by being little soluble in water.

The constitutions of the two butyric acids follow from their formation from the two isomeric propyl cyanides.

Valeric or **Pentoic Acids**, $C_5H_{10}O_2$.—Of these there are four possible isomers,

Iso-valeric Acid, $(CH_3)_2CH.CH_2.COOH$, or inactive valeric acid, occurs in various natural substances, *e.g.* dolphin and other fish oils, in valerian root, and in the bark of the wild guelder rose. It can be prepared from the iso-butyl cyanide, and from inactive amyl alcohol, by general processes. It is a mobile oily liquid, b.p. 175°, sp. gr. 0·9536 at $\underline{0^\circ}$; it smells like old cheese, is strongly acid to the taste, attacks the skin, and is little soluble in water.

Methyl-ethyl-acetic Acid,  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH.COOH$, the optically active valeric acid, from active amyl alcohol (see p. 102); boils at 175°, and its sp. gr. is 0·941 at 21°.

Ordinary **valeric acid** is a mixture of this and the above-mentioned acid.

The other isomers are **normal valeric acid,** $CH_3(CH_2)_3.COOH$, and **tri-methyl-acetic acid,** $(CH_3)_3.C.COOH$.

Higher Fatty Acids.—Many of these acids occur in nature as glyceryl esters in various fats and oils (see p. 153); but only those appear to so exist which contain an even number of carbon atoms. They are difficult to separate from each other, this being performed by fractional precipitation. The number of possible isomers for each member is great, but those naturally occurring have been shown to be normal in their structure. The two acids of greatest importance are palmitic and stearic acids.

Palmitic Acid, $C_{15}H_{31}.COOH$, is found combined with glycerin as palmitin (p. 154) in many fats and oils, such as palm and olive oils, also combined with other alcohols in bees'-wax, spermaceti, and Japan wax. It is found free in palm oil and in lycopodium spores; and can be formed by fusing cetyl alcohol with caustic potash—

$$C_{15}H_{31}CH_2OH + KOH = C_{15}H_{31}COOK + 2H_2$$

It is best prepared either by saponifying Japan wax, then liberating the acid by HCl and rectifying it; or else by separating it by fractional precipitation with magnesium acetate from the fatty acids obtained from olive oil by saponification, and decomposition of the salts by a mineral acid.

Properties.—Palmitic acid crystallises in white needles, m.p. 60·75° ; its sp. gr. (in the liquid state) is 0·853 at $\frac{62^\circ}{}$; it decomposes on heating to its boiling point, but at 100 mm. pressure its b.p. is 271·5°.

Stearic Acid, $C_{17}H_{35}.COOH$, occurs in association with palmitic and oleic acids as stearin (p. 154) in many fats, such as beef and mutton suet, and hence in tallow. These fats yield a mixture of acids; the solid acids in the mixture are separated by pressure from the oleic acid, and then repeatedly recrystallised from alcohol till the stearic acid is obtained pure.

Properties.—Stearic acid crystallises from hot alcohol in white pearly plates, b.p. 232° at 15 mm., m.p. 69·2°, and sp. gr. 1·00 at $\frac{10^\circ}{}$.

BUTTER. OILS AND FATS. SOAPS.

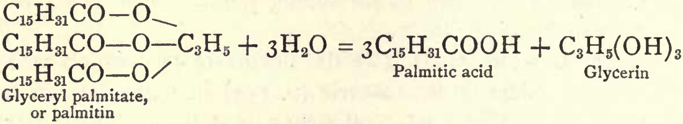
This is, perhaps, the most convenient place to discuss the constitution of the various naturally occurring oils and fats, although the reader must refer to later portions of the book for information on the properties of several of their components.

The general term "fat" is applied to a number of more or less greasy substances which are found in animal tissues or are expressed from the seeds of plants. The more liquid fats are generally spoken of as "oils."

The oils are divided into non-drying and drying oils, according as they remain unchanged on exposure to air or become oxidised to a resinous compound. Linseed oil is the best illustration of the second class.

The animal fatty tissues, such as beef or mutton suet, and the flare of the pig, yield the fat itself on heating, in a fluid form which can be separated from the membrane, and then solidifies. The vegetable fats and oils are obtained from the seeds or fruits which contain them by pressure or by extraction with solvents.

These oils and fats are non-volatile, and, when heated with acids, alkalis, or superheated steam, undergo hydrolysis or saponification, with the liberation, usually, of glycerin and fatty acids, which latter vary according to the fat or oil employed. The fundamental reaction may be illustrated by the following typical equation:—



$$\underset{\substack{\text{Glyceryl palmitate,}\\\text{or palmitin}}}{\left.\begin{array}{l}C_{15}H_{31}CO-O\\C_{15}H_{31}CO-O\\C_{15}H_{31}CO-O\end{array}\right\rangle C_3H_5} + 3H_2O = 3\underset{\text{Palmitic acid}}{C_{15}H_{31}COOH} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

If in this reaction alkalis are employed, the resultant product is not the acid, but the corresponding salt or **soap.** The fats and oils, therefore, apparently contain fatty or other acids combined with glycerin (see p. 243), or, in other words, they are **esters of the acids and glycerin.**

The principal acids found are palmitic acid, present as "palmitin," stearic acid as "stearin," and oleic acid (p. 212) as "olein," which substances are the neutral esters of glycerin and the respective acids.

Butter is the fatty constituent of milk, obtained from it by churning. It is a mixture of glycerides of butyric, caproic, palmitic, stearic, oleic, and other acids, along with a small percentage of curd and varying quantities of water. The fat can be separated from the curd by melting it in hot water, when the fat rises to the surface.

Butter differs from other fats by containing several acids which are readily soluble in hot water. This differentiates it from **oleo-margarine,** a butter substitute, which is a mixture of fats made from carefully prepared beef fat or lard, along with certain vegetable oils, and, in the higher qualities, some butter. The lower qualities are given the flavour of butter by mixing them with a certain amount of milk, and are coloured with annatto.

Soap.—Very many different oils and fats are employed in soap-making, *e.g.* palm, olive, cotton seed, sesamé, poppy, and other oils; tallow, lard, and kitchen grease among animal fats; and fish oils. These yield *hard* or *soft* soaps, according to the alkali employed.

Soft soaps are made by boiling such oils as linseed, hempseed, olive, and fish oils with potash lye, until the whole is a homogeneous mass. A certain amount of palm oil or tallow is frequently added, so that the finished product may show white nodules of potassium palmitate or stearate, which produce the appearance technically known as "figging." Soft soap contains from 30 to 50 per cent. of water, as well as the glycerin produced in the saponification. There is always, too, an excess of alkali present.

Hard soaps may be made in several ways; thus some soaps are made by neutralising the "oleine" or "red oil" obtained in stearin manufacture (p. 156) with sodium carbonate or caustic soda, and then running the soap into the cooling frames to solidify.

By far the largest quantity, however, is prepared by the saponification of some form of fat, or mixture of fat and resin. The oil is heated in a large pan, and a small quantity of weak soda lye is added, which effects a partial saponification and emulsification; stronger lye is then added till nearly the whole of the fat is saponified. If the boiling has been properly carried out, there remains then a homogeneous semi-fluid mass of partly formed soap mixed with water and glycerin in what is termed the "close" state.

This is "grained" or salted out by the addition of salt, which causes the soap to rise as a curd to the top. The spent lyes, containing salt, glycerin, and impurities, are then drawn off, and the soap is boiled with more alkaline lyes till it is quite alkaline to the taste and saponified completely. The soap paste is allowed to stand, the lyes are drawn off, and the soap heated by blowing steam through it till a certain texture, the "fit," is obtained. It is then allowed to rest, and the soap separates into three layers—at the top a frothy "fob," next "neat" or good soap, and the "niger" (aqueous liquors and impurities) at the bottom. The soap is then drawn off into the cooling frames. This method enables the maker to get an almost neutral soap, and is usually employed for soaps which contain a certain proportion of resin.

Curd soap is prepared by boiling a saponified tallow soap with water or weak lye, allowing it to stand so that impurities can settle, and then boiling it down till the flakes show the appearance desired.

Mottled soap is produced by using a mixture of fats, and, after complete saponification and settling, introducing a small amount of ultramarine or copperas before running it into the frames. The colour becomes separated in the more translucent part of the soap.

For the purpose of cheapening soap, silicate of soda is often incorporated with it, and does not lessen its detergent properties to a great extent. The composition of soap varies, but may be taken as *about* 8 per cent. of alkali, 63 per cent. of fatty acids, and 30 per cent. of water.

Soap is largely employed as a cleansing agent, for removing grease and other impurities from textile fabrics and from the body. Its action depends upon its hydrolysis by water, free alkali being formed, and an acid soap; the latter lathers and envelops the particles of dirt, removing them mechanically, while the alkali enables the solution to thoroughly wet the fabric.

Soap is also employed as a medicine, both internally and externally; it acts as a mild alkali.

Lead soap, obtained by saponifying olive oil with litharge, is employed as diachylon plaster.

"Stearin" and "Oleine."—For the purpose of candle manufacture, oils and fats are either heated with lime, the lime soap decomposed by H_2SO_4 and the fatty acids washed with water, or else they are decomposed by sulphuric acid only, and then washed. The solid stearic and palmitic acids are separated from the oleic acid by crystallisation and pressure. The solid acids form the "stearin" used in making candles, the oleic acid is the "oleine" or "red oil" referred to on p. 155.

CHAPTER XX.

ACID HALOIDS, ANHYDRIDES, ETC.

ACIDS can yield two classes of substitution compounds, viz. those in which the *hydrogen of the alkyl group* is replaced by other atoms or radicles (*e.g.* chlor-acetic acid, p. 147), and those in which the OH group is displaced by such substituents. We shall now consider examples of the latter class.

ACID CHLORIDES, BROMIDES, ETC.

Acetyl Chloride, $CH_3.COCl$, *acetic chloride*, can be obtained in a variety of ways, use being made of similar reactions to those employed in the preparation of haloid derivatives of the hydrocarbons from the alcohols; *i.e.* by the action of the chlorides of phosphorus, phosphorus oxychloride, or hydrochloric acid upon the acid or its salts.

So it is produced (*1) when PCl_5 and glacial acetic acid are distilled together—

$$CH_3.COOH + PCl_5 = CH_3.COCl + POCl_3 + HCl$$

(compare the reaction with Alcohol, p. 65). (*2) Acetyl chloride is also formed when $POCl_3$ acts upon *dry* potassium or sodium acetate—

$$2CH_3.COOK + POCl_3 = 2CH_3.COCl + KPO_3 + KCl$$

There must not be an excess of the salt, or acetic anhydride is also produced. And (*3) useful reactions for its formation are those in which PCl_3 acts either upon an acetate or the glacial acid—

$$3CH_3.COOK + PCl_3 = 3CH_3.COCl + K_3PO_3$$
$$3CH_3.COOH + 2PCl_3 = 3CH_3.COCl + P_2O_3 + 3HCl$$

In this, as in the previous case, an excess of the salt or acid causes the production of anhydride.

†*Process.*—Fit a dry distilling flask with a stoppered funnel; connect the flask tightly to a perfectly dry condenser and a tubulated receiver (the latter being fitted with a calcium chloride tube,

so as to prevent access of moisture). Place 60 grams of phosphorus tri-chloride in the flask, and carefully add 40 grams of glacial acetic acid by means of the stoppered funnel. Then heat to about 40°, and when the evolution of hydrochloric acid has nearly ceased, raise the temperature and collect the distillate, which may be purified by fractional distillation over dry sodium acetate. *The whole operation should be conducted in a good fume-cupboard, or out of doors.* Keep the acetyl chloride in well-stoppered bottles or sealed tubes.

(4) Acetyl chloride is formed when hydrochloric acid and P_2O_5 act upon acetic acid; the latter acts as a dehydrating agent.

Properties.—Acetyl chloride is a mobile, colourless, strongly refractive liquid, b.p. 50·9° (cor.), sp. gr. 1·1305 at $\frac{20^{\circ}}{4^{\circ}}$. It fumes strongly on exposure to moist air; its vapour is very pungent and irritating, and attacks the eyes and mucous membranes very violently. It is decomposed violently by water, and alcohols vigorously act upon it, hydrochloric acid being liberated; acetic acid is regenerated in the former case, and an ethereal salt formed in the latter—

$$CH_3.COCl + HOH = CH_3.COOH + HCl$$
$$CH_3.COCl + C_2H_5OH = CH_3.COOC_2H_5 + HCl$$

It can be reduced by sodium amalgam to ethyl alcohol. It reacts with sodium acetate to form acetic anhydride, and with NH_3 to form acetamide (see p. 182).

Acetyl Bromide, $CH_3.COBr$, can be obtained by the action of phosphorus and bromine upon glacial acetic acid. It is a colourless liquid, b.p. 81°, and resembles the chloride in its properties.

Acetyl Iodide, $CH_3.COI$, cannot be obtained by the action of phosphorus iodide on acetic acid; it is necessary to use either the anhydride or a salt. It is a brown transparent liquid, b.p. 105°, sp. gr. 1·98 at $\frac{17^{\circ}}{}$. It is readily decomposed by water.

The methods of preparation and general reactions of acetyl chloride with alcohols, water, ammonia, salts, etc., may be taken as quite typical of the acid haloids generally.

ACID ANHYDRIDES.

Acetic Anhydride, $(C_2H_3O)_2O$, *acetic oxide,* is formed (1), though only in small quantity, by abstracting the elements of water from glacial acetic acid with P_2O_5; (*2) by the action of acetyl chloride upon dry potassium or sodium acetate—

$$C_2H_3OCl + CH_3.CO_2Na = (C_2H_3O)_2O + NaCl$$

†*Process.*—Allow 30–50 grams of acetyl chloride to run slowly from a stoppered funnel upon an equal weight of dry sodium acetate contained in a 250 c.c. retort or flask connected with a dry condenser and receiver, as for acetyl chloride. Cool the retort till the reaction is over, distil off the anhydride from a sand-bath and rectify by distillation, collecting apart the portion which boils between 135° and 140°. By further rectification of this fraction a product boiling at 180° can be obtained.

(*3) It is also produced by acting on an acetate with PCl_3, $POCl_3$, or $COCl_2$, acetyl chloride being formed first (*q.v.*), and the previous reaction then taking place.

Process.—Add 3 parts of $POCl_3$ to 10 parts of dry sodium acetate, and distil. Rectify the distillate over sodium acetate.

Properties.—Acetic anhydride is a colourless, strongly refractive liquid, and smells somewhat like acetic acid; b.p. 137·8°, sp. gr. 1·0799 at $\underline{15{\cdot}2^\circ}$. It has *no* acid reaction if pure; is insoluble in water, but, if allowed to stand with that body, eventually combines to form acetic acid; with alcohols it yields esters. It is readily acted upon by alkalis and alkaline earths, with the formation of acetates. Gaseous HCl reacts with it to form acetic acid and acetyl chloride—

$$(CH_3CO)_2O + HCl = CH_3.COCl + CH_3.COOH$$

Chlorine forms a mixture of acetyl chloride and chlor-acetic acid, bromine acts similarly, while iodine has no action. It differs from acetic acid by decolourising potassium permanganate, and giving a mirror with an ammoniacal solution of $AgNO_3$. It yields aldehyde and then alcohol when reduced by sodium amalgam.

Detection of Hydroxyl.—It has been pointed out already that acetyl chloride and acetic anhydride both act on alcohols, forming ethereal acetates, and, generally speaking, the former reacts with all organic compounds which contain OH, NH_2, or NH groups, and if there is no evolution of HCl on its addition, those radicles may be assumed to be absent. In the absence of the two latter groups, the property that the chloride and anhydride have of reacting with hydroxyl is used to show its presence, and to determine how many times that radicle occurs in the molecule.

An alcohol may be treated directly with acetyl chloride, or warmed with acetic anhydride and dried sodium acetate. In both cases fragrant esters are formed, which can readily be separated. In the case of an alcoholic acid (*i.e.* an acid which contains an alcoholic group, *e.g.* $CH_2OH.COOH$) the COOH group must itself be esterified before the alcoholic groups are treated with the above compounds.

The *number* of acetyl groups introduced cannot be ascertained by elementary analysis. For this purpose the ester is purified, a known weight of it saponified, and the amount of acetic acid thus freed is estimated; from this amount the number of radicles can be calculated, since one molecule of acetic acid corresponds to one hydroxyl group.

ESTERS OF THE FATTY ACIDS WITH MONOHYDRIC ALCOHOLS.

Just as when the alcohols act upon inorganic acids ethereal salts are produced, so similarly they form esters with organic acids, some of which are of interest.

Methyl Acetate, $CH_3.COOCH_3$, occurs in crude wood vinegar, and is a fragrant colourless liquid, which boils at 57·5°.

Ethyl Acetate, $CH_3.COOC_2H_5$, *acetic ether*, is formed (*1) by the direct action of ethyl alcohol on acetic acid—

$$CH_3.COOH + C_2H_5OH = CH_3CO.OC_2H_5 + H_2O$$

but, as we have already seen (p. 119), the reaction is not complete. (*2) The method usually employed in its preparation depends upon the action of H_2SO_4 on a mixture of an acetate and the alcohol, which is, after all, a modification of the first reaction, and probably depends upon the following reactions:—

$$\text{(i.)} \quad C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O$$
$$\text{(ii.)} \quad C_2H_5HSO_4 + CH_3.COONa = CH_3.COOC_2H_5 + NaHSO_4$$

†*Process.*—Mix together[1] 90 grams of concentrated H_2SO_4 and 36 grams of 95 per cent. alcohol. Allow the mixture to stand for 24 hours, and then pour it on to 60 grams of previously fused and dried sodium acetate, which is broken into small pieces and placed in a flask, which must be kept cool by surrounding it with water. Allow the mixture to stand for 12 hours, and then distil from a sand-bath, and collect the distillate till only water comes over. Shake the distillate with a strong solution of Na_2CO_3, separate, then dry over fused $CaCl_2$ and rectify by distillation, collecting that which distils between 74° and 78°. The distillate is nearly pure ethyl acetate, and may be purified by redistillation.

Properties.—Ethyl acetate is a colourless liquid with a fragrant and refreshing odour, sp. gr. $0{\cdot}9072$ at $\frac{15^\circ}{15^\circ}$, b.p. $77{\cdot}5^\circ$. It mixes readily with alcohol and ether, and is moderately soluble in water. When dry it is stable, but if moist it gradually undergoes saponification, which of course takes place more readily in presence of alkalis—

$$CH_3.COOC_2H_5 + NaOH = CH_3.COONa + C_2H_5OH$$

When heated with sodium a rather complicated reaction takes place, which results in the production of a compound called aceto-acetic ester, which has been of great service in the synthetical formation of various acids and ketones (see Appendix, p. 281). Commercial "acetic ether" is usually a very impure substance, and contains considerable quantities of alcohol, acetic acid, water, etc.

GENERAL REMARKS.

Esters of organic acids may be produced as just illustrated, viz. (1) from the acid and the alcohol; (2) from a salt of the acid, H_2SO_4 and the alcohol. They are also formed (3) when acid chlorides or acid anhydrides act upon the alcohol—

$$C_2H_3OCl + C_2H_5OH = C_2H_3O.OC_2H_5 + HCl$$

---

[1] The best way to mix these is to pour the alcohol down a thistle funnel into the acid while stirring constantly with the stem of the funnel.

and (4) difficultly volatile or non-volatile ethers may be produced by passing gaseous HCl into a mixture of the alcohol and the acid.

Properties.—The esters of organic acids are liquid or solid bodies, which are usually insoluble in water. They may be saponified by heating with water, alkalis, or dilute acids. When acted upon by ammonia, *acid amides* and the alcohols are produced.

Many of these esters possess characteristic fruity odours, and are employed as artificial fruit essences; thus—

Ethyl Formate, $H.CO.OC_2H_5$, finds employment in flavouring rum and arrack;

Amyl Acetate, prepared from iso-amyl alcohol (p. 101), possesses a pear-like odour, and is used in alcoholic solution as jargonelle pear essence;

Ethyl Butyrate in alcoholic solution is pine-apple oil; and **Amyl Valerate** is used as "apple oil."

CHAPTER XXI.

COMPOUNDS OF THE ALCOHOLIC (ALKYL) RADICLES WITH NITROGEN.

THE three elements nitrogen, phosphorus, and arsenic belong, as the student will remember, to the same group, and many of the compounds formed by one element in the group very considerably resemble similar compounds formed by the others. Thus each of the three elements named combines with three atoms of hydrogen to form respectively ammonia, NH_3, phosphine, PH_3, and arsine, AsH_3. The hydrogen in these can be more or less readily replaced by alcoholic radicles, and in this manner very important series of compounds are produced, which show similar differences in character to the parent hydrides. Thus ammonia is strongly alkaline, phosphine is less so, and arsine only faintly alkaline; and the ethyl derivatives of these substances show a like gradation of properties.

AMINES, AND AMMONIUM BASES.

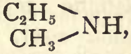
Amines.—The term "amine" is applied to compounds which are derived from ammonia by the replacement of its hydrogen by alkyl radicles. If they are derived from one molecule of ammonia, they are called **mon-amines**; if from two molecules, **di-amines**; and if from three molecules, **tri-amines.**

It is possible to replace either one, two, or three atoms of hydrogen in ammonia by alkyl groups. If one atom only is replaced, there is produced a **primary amine** or **amido base,** characterised by the amido group NH'_2, *e.g.* $NH_2.CH_3$; if two atoms undergo substitution, a **secondary amine** or **imido base** containing the imido group NH'' is formed, *e.g.* $NH(CH_3)_2$; while if three groups are introduced, and nitrogen only remains, a **tertiary amine** or **nitrile base** is produced, *e.g.* $N(CH_3)_3$.

The hydrogen atoms are not of necessity all replaced by the *same* radicles, for it is possible to introduce three different monad groups into the molecule at once. Dyad or triad radicles may also be employed, so that complex amines can be produced with ease, and the number of possible isomers may thus be very considerable.

For example, the formula C_3H_9N may represent either—

$C_3H_7NH_2$, Propylamine



$\left.\begin{array}{l}C_2H_5\\CH_3\end{array}\right\rangle NH$, Methyl-ethylamine

or $(CH_3)_3N$ Trimethylamine

The likeness of the amines to ammonia is supported by the formation from them of compounds which are analogous to the ammonium compounds, *e.g.* the **quaternary compounds** $N(CH_3)_4I$ and $N(CH_3)_4OH$ (the tetra-methyl ammonium iodide and hydroxide) are analogous to the ammonium compounds NH_4I and NH_4OH respectively.

In studying the amines it will be convenient to discuss first one of the general reactions, because certain methods of production apply to all four kinds of amido derivatives.

Thus, consider the action of alcoholic ammonia upon alkyl haloids when they are heated together in closed tubes. It may be illustrated by the equations that represent the interaction of ammonia and ethyl iodide, in which the hydrogen atoms of the ammonia are successively replaced by ethyl—

$$\begin{aligned}
&\text{(i.)} & NH_3 + C_2H_5I &= NH_2(C_2H_5).HI \\
&\text{(ii.)} & NH_2(C_2H_5) + C_2H_5I &= NH(C_2H_5)_2.HI \\
&\text{(iii.)} & NH(C_2H_5)_2 + C_2H_5I &= N(C_2H_5)_3.HI \\
&\text{(iv.)} & N(C_2H_5)_3 + C_2H_5I &= N(C_2H_5)_4I
\end{aligned}$$

or, from another standpoint, the latter phases may be represented—

$$\begin{aligned}
&\text{(ii.)} & NH_2(C_2H_5).HI + NH_3 + C_2H_5I &= NH(C_2H_5)_2.HI + NH_4I \\
&\text{(iii.)} & NH(C_2H_5)_2.HI + NH_3 + C_2H_5I &= N(C_2H_5)_3.HI + NH_4I \\
&\text{(iv.)} & N(C_2H_5)_3.HI + NH_3 + C_2H_5I &= N(C_2H_5)_4I + NH_4I
\end{aligned}$$

It is only possible by this method to prepare a mixture of bases. In the case cited ethylamine hydriodide is chiefly formed; when methyl iodide is employed, the tetramethyl ammonium iodide is mainly produced.

The bases are separated from each other as follows. The alcoholic solution is filtered; the residue is NH_4I. The filtrate is distilled with KOH, when the *amines* distil over; the tetraethyl ammonium iodide remains behind unaffected. The distillate is dried over solid KOH, and dry ethyl oxalate then carefully added; it is then heated to 100° for some time. Ethylamine and diethylamine respectively form diethyloxamide and diethyloxamic ester, while the triethylamine undergoes no change, and can be distilled off. The *solid* oxamide is separated by pressure from the oxamic ester, or else washed out from it with water. The two substances are then separately distilled with potash, and yield free ethylamine and diethylamine respectively.

The above reactions are employed when large quantities of the ethylamines are required, the impure ethyl chloride produced in chloral manufacture being used instead of C_2H_5I

Process.—1 part of the crude chloride is mixed with 3 parts of 95 per cent. alcohol, saturated with NH_3 at 0°, and digested in a closed wrought-iron vessel surrounded by boiling water for 1 hour. On cooling, NH_4Cl separates, and the residual liquid is distilled, the alcohol, NH_3, etc., collected. KOH is added to the residue, and the layer of bases is dried by solid NaOH, and treated as described above.

PRIMARY MONAMINES.

The general properties of the monamines will be illustrated mainly (though not entirely) by the ethyl derivatives.

Methylamine, CH_3NH_2, found in herring-brine, is a product of the distillation of woody and animal matter, and so is found in crude wood spirit. It can be synthetically prepared in several ways besides that indicated on p. 163. A typical method is that in which acetamide (p. 182) is treated with bromine, and then with caustic potash or soda; the methylamine is formed thus—

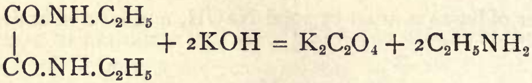
$$CH_3.CONH_2 + Br_2 + KOH = \underset{\text{Acetbromamide}}{CH_3.CONHBr} + KBr + H_2O$$

$$CH_3.CONHBr + 3KOH = CH_3NH_2 + K_2CO_3 + KBr + H_2O$$

†*Process.*—Mix 20 grams acetamide with 54 grams bromine; keep it cool, and add a 10 per cent. solution of 20 grams KOH till it is nearly decolourised. Then run this from a stoppered funnel into a 500 c.c. distilling flask which contains a 30 per cent. solution of 60 grams KOH, heated to 60–70°. Digest for 15 minutes, then boil, and receive the methylamine vapour in hydrochloric acid. Evaporate the solution to dryness, extract the methylamine salt from the NH_4Cl with hot absolute alcohol and allow to crystallise. On warming these crystals with KOH, the methylamine is liberated as an inflammable gas.

Properties.—Methylamine is a colourless gas condensible to a liquid, b.p. $-6°$, and not solid at $-75°$. It is the most soluble of all gases; 1 volume of water at 12·5° dissolves 1150 volumes of it. Its odour is ammoniacal and fish-like. Its solution is strongly caustic and alkaline, and precipitates many salts similarly to NH_4HO, but differs from that body by not dissolving the hydroxides of cadmium, nickel, and cobalt. It forms salts similarly to ammonia. The hydrochloride forms deliquescent leaflets soluble in water, and gives double salts with $PtCl_4$ and $AuCl_3$.

Ethylamine, $C_2H_5NH_2$, is produced (*1) from ethyl iodide and NH_3 as described on p. 163—the di-ethyl oxamide being decomposed as follows :—



$$\begin{array}{l} \mathrm{CO.NH.C_2H_5} \\ | \\ \mathrm{CO.NH.C_2H_5} \end{array} + 2\mathrm{KOH} = \mathrm{K_2C_2O_4} + 2\mathrm{C_2H_5NH_2}$$

The di-ethyloxamide (p. 164), after recrystallisation from water, yields it pure. It is also obtained (*2) from propionamide $C_2H_5CONH_2$ (compare Methylamine); and (*3) by reduction of nitro-ethane, which is a very characteristic method of formation of amines—

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O$$

and (*4) by the decomposition of ethyl iso-cyanate or cyanurate with KOH—

$$CONC_2H_5 + 2KOH = C_2H_5NH_2 + K_2CO_3$$

Properties.—Ethylamine is a colourless, mobile, inflammable liquid, b.p. 19°, which does not solidify at $-140°$, sp. gr. 0·696. It is hygroscopic, has a strong ammoniacal odour, caustic taste, and alkaline reaction, and absorbs moist CO_2 with the formation of a salt, probably a carbamate. It dissolves in water with evolution of heat, and is separated from its solution by KOH or K_2CO_3. It separates NH_3 from its salts; like methylamine, it precipitates many metallic hydroxides, but differs from that and NH_3 by dissolving aluminium hydroxide. It is readily decomposed by nitrous acid, with formation of ethyl alcohol (see p. 168)—

$$C_2H_5NH_2 + HNO_2 = C_2H_5OH + H_2O + N_2$$

and gives the carbamine reaction with chloroform and alcoholic KOH (see p. 195).

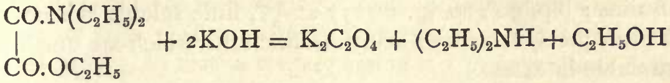
It forms salts, which differ from ammonium compounds by their greater solubility in alcohol. The hydrochloride, $C_2H_5NH_2.HCl$, forms deliquescent plates, and gives an orange crystalline double salt with $PtCl_4$, $2(C_2H_5NH_2HCl).PtCl_4$, also a yellow double salt with $AuCl_3$, $C_2H_5NH_2HCl.AuCl_3$.

SECONDARY MONAMINES.

Dimethylamine, $(CH_3)_2NH$, occurs in Peruvian guano; and can be obtained from the mixture of bases formed by the action of ammonia on methyl iodide.

Properties.—It is a very volatile inflammable liquid, b.p. 7·2°, is strongly alkaline, and forms a characteristic yellow precipitate with picryl chloride, $C_6H_2(NO_2)_3Cl$.

Diethylamine, $(C_2H_5)_2NH$, is obtained by the action of NH_3 upon ethyl iodide, bromide, or chloride (p. 163), then forming diethyloxamic ester (p. 164), and distilling it with KOH—



$$\begin{array}{l} CO.N(C_2H_5)_2 \\ | \\ CO.OC_2H_5 \end{array} + 2KOH = K_2C_2O_4 + (C_2H_5)_2NH + C_2H_5OH$$

Properties.—It is a colourless inflammable liquid, b.p. 56°, sp. gr. 0·726 at 0°. Its smell is strongly ammoniacal; it is alkaline, readily soluble in water, and differs from ethylamine in not redissolving the precipitate it gives with zinc salts. It reacts with HNO_2, forming diethyl-nitrosamine (see p. 168) (difference from ethylamine). Its hydrochloride forms non-deliquescent plates, and the platinum double salt forms orange crystals, $[N(C_2H_5)_2H.HCl]_2PtCl_4$.

TERTIARY MONAMINES.

Trimethylamine, $(CH_3)_3.N$, is found in herring-brine, in the juices of many plants, such as *Arnica montana*, in hawthorn and pear bloom, in guano and many other animal substances. It can be produced from methyl iodide by the reactions and separation illustrated on p. 164.

Manufacture.—Large quantities can be prepared from *vinasse*, a residue obtained in beet-root sugar manufacture (see p. 80). This is distilled, and the distillate condensed in sulphuric acid. Trimethylamine and ammonium sulphates are formed, and the latter separated by crystallisation. The mother liquor is distilled with lime and the distillate neutralised by HCl. On crystallising, NH_4Cl separates, and the mother liquor contains the hydrochloride of the base, from which impure trimethylamine can be separated by an alkali.

Properties.—Trimethylamine is a liquid, b.p. 3·5°, sp. gr. 0·662 at −5°. It has a penetrating fish-like smell, is soluble in water, and easily combustible.

Uses.—It finds employment in producing potassium carbonate by a process quite analogous to the ammonia-soda process, and is used because $KHCO_3$ and NH_4Cl differ little in solubility, while $(CH_3)_3N.HCl$ is much more soluble than the latter salt.

Triethylamine, $(C_2H_5)_3N$, formed from ethyl iodide (p. 164) or by the distillation of tetra-ethyl ammonium hydroxide (*q.v.*), is a colourless, oily liquid, inflammable, and strongly alkaline; b.p. 90°, sp. gr. 0·7277 at $\frac{20^\circ}{4^\circ}$, little soluble in water. It gives precipitates with many metallic salts, which are usually insoluble in excess.

Diagnosis of Amines.—One method of separating the three classes of amines has been already illustrated in their separation, given on p. 164. Other methods of distinction are the following:—

All primary amines give the iso-nitrile reaction with alcoholic KOH and $CHCl_3$ (see p. 195)—

$$C_2H_5NH_2 + CHCl_3 + KOH = C_2H_5NC + 3KCl + 3H_2O$$

and they also are characteristically decomposed by nitrous acid, with *liberation of nitrogen*, e.g.—

$$C_2H_5NH_2 + HNO_2 = N_2 + C_2H_5OH + H_2O$$

As a nitrite is presumably first formed, this reaction is analogous to the decomposition of ammonium nitrite by heat—

$$NH_4NO_2 = N_2 + HOH + H_2O$$

They also readily yield mustard oils, *e.g.* C_2H_5NCS, by successive treatment with CS_2 in alcohol and then aqueous ferric chloride (see p. 199).

Secondary amines react with HNO_2 to form **nitrosamines,** *e.g.*—

$$(C_2H_5)_2NH + HNO_2 = \underset{\text{Diethyl-nitrosamine}}{(C_2H_5)_2N.NO} + H_2O$$

which are neutral oils that reproduce the amine on reduction with Sn and HCl. The nitrosamines give a dark green solution when mixed with concentrated H_2SO_4 and phenol. This becomes red when diluted, and excess of alkali produces an intense blue or green shade.

Finally, **tertiary amines** are unchanged by nitrous acid.

GENERAL REMARKS ON THE AMINES.

The methods of formation already illustrated are all of general application for the production of amines.

Properties.—The lower members of the amine series are gases; the higher are liquids, most of which are volatile either alone or in a current of steam. They greatly resemble ammonia, but are more strongly basic, and can expel ammonia from its salts. Their basicity increases with the number of alkyl groups, so that a tertiary amine is a stronger base than a secondary, and that than a primary one. They form salts with acids, and their hydrochlorides combine with $PtCl_4$ or $AuCl_3$ to form double salts; they can also replace ammonia in alums. Their other reactions have already been sufficiently illustrated.

QUATERNARY OR AMMONIUM COMPOUNDS.

The amine bases unite with acids to form true ammonium salts, and they also unite with alkyl haloids to form tetra-alkylated ammonium compounds, of which the **tetra-methyl** and **tetra-ethyl ammonium iodides** have been mentioned (pp. 163 and 164). These salts, though not affected by boiling alkalis (p. 164), yield, by the action of moist silver oxide, the ammonium hydroxide derivative.

Tetra-methyl Ammonium Hydroxide, $(CH_3)_4NOH$, and **Tetra-ethyl Ammonium Hydroxide,** $(C_2H_5)_4NOH$, are so formed from the corresponding iodides; *e.g.*—

$$(C_2H_5)_4NI + AgOH = (C_2H_5)_4NOH + AgI$$

On evaporation *in vacuo* both the hydroxides are obtained as crystalline substances, which absorb water and CO_2 from the air. They are both strongly caustic bodies, resembling caustic potash in their properties, and saponify fats. When neutralised with acids, they form salts.

HYDRAZINES.

Just as amines may be looked upon as derivatives of ammonia, NH_3, so there exist substances, termed **hydrazines,** which appear to be derived from **hydrazine** or **di-amidogen,** $NH_2.NH_2$.

This latter substance is not known free, but only as a hydrate and in its salts. Its fatty derivatives are strong bases, thus resembling the amines, and can unite with either one or two equivalents of acids to form salts. They differ from the amines by being powerful reducing agents, *e.g.* they reduce Fehling's solution.

CHAPTER XXII.

COMPOUNDS OF PHOSPHORUS AND ARSENIC WITH ALKYL RADICLES.

COMPOUNDS OF PHOSPHORUS; PHOSPHINES, ETC.

Phosphines.—Primary, secondary, and tertiary phosphines corresponding to the amines can be prepared, but the principal methods employed differ from those used for the analogous nitrogen compounds. One of the chief substances required for the formation of the phosphorus derivatives is—

Phosphonium Iodide, PH_4I, which can be formed, amongst other ways, (1) by direct union of PH_3 with HI; (2) by decomposing PI_3 with a *little* water—this being the usual method of manufacture.

†*Process.*—Place in a 200 c.c. retort 40 grams of ordinary phosphorus and the same weight of CS_2; next add 68 grams of iodine to this solution, keeping it carefully cooled. When the reaction is over, distil off *all* the CS_2 on a water-bath; then connect the retort with a CO_2 apparatus, and with a wide condensing tube with a globe receiver and condensing bottles, as arranged in Fig. 42. The first condensing bottle contains dilute HI, and the other water. A slow current of CO_2 is now *continuously* passed through the apparatus, and the retort is gently heated, while 24 grams of water are *slowly* added by the drop funnel. The heat of the reaction sublimes most of the PH_4I into the tube and the globular receiver, while the HI is absorbed in the condensing bottles. The operation is complete in about 8 hours, and towards its close the

retort will require more strongly heating. When no more sublimation occurs, the tube is disconnected, one end is corked up, and the PH_4I is raked out with a wire into dry stoppered bottles.

The reaction may be expressed by the equation—

$$13P + 9I + 21H_2O = 7PH_4I + 3H_4P_2O_7 + 2HI$$

Properties.—Phosphonium iodide crystallises in glittering transparent prisms; it boils at about 80°, and may be sublimed in HI. It is a powerful reducing agent, and frequently finds employment in organic chemistry on that account; but its chief use is for the preparation of phosphines and phosphonium compounds (see below).

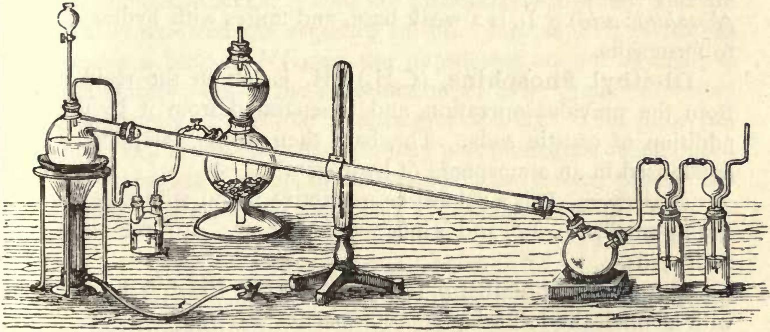


FIG. 42.

The phosphines will be illustrated by the ethyl derivatives, and their properties and preparations should be carefully compared with those of the corresponding amines; their behaviour on oxidation should be especially noted.

Ethyl Phosphine, $C_2H_5PH_2$, is formed when ethyl iodide, phosphonium iodide, and zinc oxide are heated in a closed tube for 6–8 hours to 150°. The reaction is complicated, but salts of ethyl and diethyl phosphine are principally formed thus—

$$2C_2H_5I + 2PH_4I + ZnO = 2C_2H_5PH_2.HI + ZnI_2 + H_2O$$

and—

$$2C_2H_5I + PH_4I + ZnO = (C_2H_5)_2PH.HI + ZnI_2 + H_2O$$

Both substances form compounds with the zinc iodide. The mixture of substances is treated with water in presence of hydrogen. The water decomposes the salt of the primary base into the free base and HI—

$$C_2H_5PH_2.HI + xH_2O = C_2H_5PH_2 + HI + xH_2O$$

The ethyl phosphine is condensed by a freezing mixture.

Properties.—It is a strongly refractive liquid, b.p. 25°, has an overpowering odour and a bitter taste. It is readily inflammable, ignites with Cl, Br, or HNO_3, and in the latter case forms **ethane phosphonic acid,** $C_2H_5PO(OH)_2$ (*ethyl phosphinic acid*). It is a weak base, and unites with hydracids to form salts.

Di-ethyl Phosphine, $(C_2H_5)_2PH$, is left in the residue from the previous operation, and is separated from it by the addition of caustic soda. The base then distils over, and is condensed in an atmosphere of hydrogen.

Properties.—It is a colourless, refractive liquid, with a penetrating smell, b.p. 85°, and is inflammable in air. It forms salts with acids.

Tri-ethyl Phosphine, $(C_2H_5)_3P$.—When PH_4I is heated with alcohol, the following reaction occurs :—

$$PH_4I + C_2H_5OH = PH_3 + C_2H_5I + H_2O$$

but if the reaction takes place under pressure, the interaction of the PH_3 and C_2H_5I produces a mixture of $(C_2H_5)_3P.HI$ and tetra-ethyl phosphonium iodide $(C_2H_5)_4PI$ (compare formation of Amines, p. 164).

Similarly, if PH_4I and C_2H_5I are heated together, the mixture is obtained, but the primary and secondary phosphines are absent—

$$PH_4I + 3C_2H_5I = (C_2H_5)_3P.HI + 3HI$$
$$(C_2H_5)_3P.HI + C_2H_5I = (C_2H_5)_4PI + HI$$

Caustic soda frees the tertiary compound (compare the Amines) from the mixture. Tri-ethyl phosphine is also conveniently produced by the action of zinc methyl on PCl_3 :—

$$2PCl_3 + 3(C_2H_5)_2Zn = 2(C_2H_5)_3P + 3ZnCl_2$$

Properties.—It is a colourless, mobile liquid, b.p. 128°, with a suffocating odour, which, diluted, smells like hyacinths. It is insoluble in water, soluble in alcohol and ether. It absorbs oxygen from the air very rapidly, becoming acid, although it is neutral when pure, and forms tri-ethyl phosphine oxide, $(C_2H_5)_3PO$; with sulphur it forms the beautifully crystalline sulphide, $(C_2H_5)_3PS$; and with CS_2 it forms characteristic red crystals of $(C_2H_5)_3P.CS_2$. Its salts are crystalline, but deliquescent.

The phosphines (with the exception of methyl phosphine, which is a gas) are colourless, refractive, volatile liquids with an unpleasant smell. They are little soluble in water, and are readily oxidised on exposure to air. Just as PH_3 is not so strong a base as NH_3, so the phosphines are not so basic as the amines; but as the introduction of alkyl groups increases the basicity of NH_3, so it does that of PH_3. Thus phosphonium iodide and the salts of primary phosphines are decomposed by water, but the salts of the secondary and tertiary phosphines require the use of an alkali (see Phosphines above).

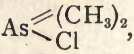
PHOSPHONIUM COMPOUNDS.

Tri-ethyl phosphine combines with C_2H_5I to form **tetra-ethyl phosphonium iodide,** exactly as tri-ethylamine forms tetra-ethyl ammonium iodide. It is also formed when PH_4I acts on C_2H_5I. When it is digested with water and freshly precipitated Ag_2O, the iodine is replaced by hydroxyl, and **tetra-ethyl phosphonium hydroxide** is formed; when this solution is dried over concentrated H_2SO_4, a bitter alkaline deliquescent crystalline mass remains, which absorbs CO_2 and behaves towards metallic solutions very much like caustic potash, but does not dissolve the oxides of zinc and aluminium so readily.

COMPOUNDS OF ARSENIC; ARSINES.

Arsenic unites with alkyl radicles to form compounds which have many analogies to those produced from nitrogen, *but apparently bodies analogous to primary and secondary amines cannot exist.*

The arsenic compounds may be best looked upon as derived from arsenic tri-chloride by the replacement of one, two, or three atoms of chlorine by alkyl radicles. The groups $AsCH_3$ and $As(CH_3)_2$ thus formed act as basic di- and mono-valent compound radicles respectively.

$AsCl_3$ yields	 $As\begin{matrix}CH_3\\Cl_2\end{matrix}$,	 $As\begin{matrix}(CH_3)_2\\Cl\end{matrix}$, and	$As(CH_3)_3$
Arsenic tri-chloride	Methylarsine di-chloride	Dimethyl-arsine chloride	Trimethyl-arsine

These compounds can unite with a molecule of chlorine to form bodies in which the arsenic is penta-valent, and that decompose on heating with the loss of CH_3Cl; *e.g.*—

$$As(CH_3)_3Cl_2 = CH_3Cl + As(CH_3)_2Cl$$

Bodies analogous to the ammonium derivatives are also known.

The methyl arsenic compounds will be taken as types, and it is convenient to reverse our general order of studying these substances, and take the tertiary derivatives first.

TERTIARY ARSINES.

Trimethylarsine, $As(CH_3)_3$, is formed (1) when arsenic tri-chloride is heated with zinc methyl (compare formation of Tri-alkyl phosphines from PCl_3)—

$$2AsCl_3 + 3Zn(CH_3)_2 = 2As(CH_3)_3 + 3ZnCl_2$$

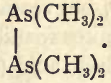
or (2) by heating sodium arsenide with methyl iodide to 180°—

$$AsNa_3 + 3CH_3I = As(CH_3)_3 + 3NaI$$

Also from tetra-methyl arsonium iodide (*q.v.*) by heating with KOH (difference from amines and phosphines).

Properties.—It is a disagreeable-smelling, refractive liquid, boiling below 100°, insoluble in water. It absorbs oxygen from the air, forming a crystalline oxide (see Tertiary phosphines). It does not unite with acids to form salts, thus differing from amines and phosphines; but, like them, it forms quaternary compounds with alkyl iodides.

DIMETHYLARSINE (CACODYL) DERIVATIVES.

It has been pointed out above that the group $As(CH_3)_2$ appears to act as a mono-valent compound radicle, which occurs as **tetra-methyl di-arsine** or **cacodyl**[1]  $\begin{matrix}As(CH_3)_2\\ |\\ As(CH_3)_2\end{matrix}$. The starting-point for the formation of cacodyl itself and its derivatives is **alcarsin,** an impure form of cacodyl oxide, obtained by heating arsenic tri-oxide with an equal weight of dry potassium acetate, condensing the vapours, and collecting the oily distillate under water, because it is spontaneously inflammable owing to the presence of free cacodyl.

$$As_2O_3 + 4CH_3.COOK = [As(CH_3)_2]_2O + 2K_2CO_3 + 2CO_2$$

Other poisonous gases are evolved, and the operation must be conducted in a good draught. When the crude distillate is distilled with several times its weight of mercuric chloride and hydrochloric acid, **cacodyl chloride** is obtained, from which its other compounds can be obtained in a pure state.

Cacodyl Chloride, $As(CH_3)_2Cl$, *dimethylarsine chloride,* is obtained as just described, or by heating trimethylarsine di-chloride—

$$(CH_3)_3AsCl_2 = (CH_3)_2AsCl + CH_3Cl$$

Properties.—It is a colourless, heavy oil, boiling near 100°, which does not fume in air, although its vapour ignites spontaneously. Its smell is stupefying, and its vapour attacks the mucous membrane most violently. It unites with $PtCl_4$ to form a compound, $2As(CH_3)_2Cl.PtCl_4$, forms double salts with other metallic chlorides, and combines with a molecule of chlorine to form cacodyl tri-chloride, $As(CH_3)_2Cl_3$, which decomposes at 40°, and forms $As(CH_3)Cl_2$ and CH_3Cl.

Cacodyl Oxide, $[As(CH_3)_2]_2O$, *tetra-methyldiarsine oxide,* is found in an impure condition in **alcarsin,** and is obtained pure by distilling the chloride with potash—

$$2As(CH_3)_2Cl + 2KOH = [As(CH_3)_2]_2O + 2KCl + H_2O$$

Properties.—It is a heavy oil, boiling about 150°, and solidifying at $-25°$. It has a frightful odour, attacks the mucous membrane, and produces insensibility. It is insoluble in

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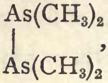
[1] From κακώδης, stinking, because of the disgusting odour it and its derivatives possess.

water, but readily soluble in alcohol or ether; it is a weak base, but unites readily with acids to form salts. Oxidation produces cacodylic acid (*q.v.*).

Besides the above, other salts of cacodyl are **cacodyl cyanide,** $As(CH_3)_2CN$, a crystalline solid formed from the chloride by treatment with $Hg(CN)_2$; and **cacodyl sulphide,** $[As(CH_3)_2]_2S$, an oily inflammable liquid, obtained when the chloride is distilled with $Ba(SH)_2$.

The free base **cacodyl,**  $\begin{array}{c} As(CH_3)_2 \\ | \\ As(CH_3)_2 \end{array}$, *tetra-methyl diarsine,* is readily formed from the chloride by heating it with zinc filings to 90–100° in a current of CO_2—

$$2As(CH_3)_2Cl + Zn = [As(CH_3)_2]_2 + ZnCl_2$$

The preparation is difficult, owing to the great inflammability of the compound.

Properties.—Cacodyl is a spontaneously inflammable, colourless, mobile liquid, b.p. about 170°, and solidifying at $-6°$. It has a frightful odour, which induces vomiting. It combines with chlorine to form the chloride, and with sulphur to form the sulphide, and with nitric acid it produces the nitrate; in fact, it acts in many ways like an element.

Cacodylic Acid, $As(CH_3)_2O.OH$, *di-methyl arsinic acid,* is produced when cacodyl oxide is oxidised in the air or by mercuric oxide and water—

$$[As(CH_3)_2]_2O + 2HgO + H_2O = 2As(CH_3)_2O.OH + 2Hg$$

It crystallises in prisms, which are deliquescent and easily soluble in water, insoluble in ether. It is not acted upon by nitric acid or by aqua regia; it forms salts with metallic oxides, which are difficultly crystallisable.

METHYLARSINE COMPOUNDS.

Methylarsine Di-chloride, $AsCH_3Cl_2$, is formed by the decomposition of cacodyl tri-chloride $As(CH_3)_2Cl_3$ by heat (p. 174), and by heating cacodylic acid in gaseous hydrochloric acid—

$$As(CH_3)_2O.OH + 3HCl = AsCH_3Cl_2 + CH_3Cl + 2H_2O$$

Properties.—It is a heavy, mobile liquid, b.p. 133°, does not fume in air, and is not decomposed by water. Its vapour attacks the mucous membrane most violently. It unites directly with chlorine to form $As(CH_3)Cl_4$. Treated with aqueous potassium carbonate, methylarsine oxide, $AsCH_3O$, is formed, a solid soluble in water, and smelling like asafœtida. When moist silver oxide acts on the dichloride in presence of water, or mercuric oxide acts on the oxide, methyl arsinic acid (methane arsonic acid), $CH_3AsO(OH)_2$, is produced.

ARSONIUM COMPOUNDS.

Tetra-methyl Arsonium Iodide, $(CH_3)_4AsI$, results (1) from the direct addition of methyl iodide to tri-methyl arsine; and (2) is the main product of the action of $AsNa_3$ upon CH_3I, and remains behind when the other products are distilled off. It is a white crystalline solid, which, on treatment with moist silver oxide, yields—

Tetra-methyl Arsonium Hydroxide, $(CH_3)_4AsOH$, which is a strongly alkaline deliquescent substance that forms salts with acids, and liberates ammonia from its salts.

CHAPTER XXIII.

COMPOUNDS OF SILICON, ZINC, AND MERCURY, WITH ALKYL RADICLES.

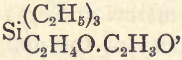
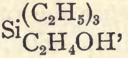
COMPOUNDS OF SILICON.

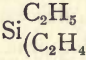
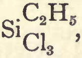
THE element silicon has already been found, in the study of inorganic chemistry, to yield many compounds which are the analogues of those given by carbon, and although our knowledge is still very imperfect, much has been done which shows that this analogy is very marked in its organic derivatives. Thus it forms compounds which are similar to hydrocarbons, alcohols, etc. Amongst these may be noted—

Silicon Methyl, $Si(CH_3)_4$, *silicon tetra-methide, tetra-methyl-silicane*, and **Silicon Ethyl,** $Si(C_2H_5)_4$, *silicon tetra-ethide, tetra-ethyl-silicane.*—These bodies, which are analogous to the hydrocarbons, tetra-methyl-methane, and tetra-ethyl-methane, can be formed by heating silicon tetra-chloride respectively with zinc methyl or zinc ethyl—

$$SiCl_4 + 2Zn(CH_3)_2 = Si(CH_3)_4 + 2ZnCl_2$$

Silicon methyl is a mobile, inflammable oil, which boils at 31°; and it is not acted upon by water, KOH, or HNO_3.

Silicon ethyl is an oil similar to the last named, sp. gr. 0·834, boiling at 153°. Chlorine acts upon it with the formation of a mono-chlor-substitution product, silico-nonyl chloride, $(C_2H_5)_3Si.C_2H_4Cl$; this, in its turn, by alternate treatment with alcoholic potassium acetate and alcoholic potash, yields first an acetate,  $\mathrm{Si}^{(C_2H_5)_3}_{C_2H_4O.C_2H_3O}$, and then the so-called **silico-nonyl alcohol,**  $\mathrm{Si}^{(C_2H_5)_3}_{C_2H_4OH}$, an oily liquid, which boils at 190°.

A number of other compounds are known which resemble alcohols or ethers, of these may be mentioned—**ethyl silicon tri-ethylate,**  $\mathrm{Si}^{C_2H_5}_{(C_2H_4OH)_3}$, a liquid which yields, by successive treatment with acetyl chloride and water, **ethyl silicon tri-chloride,**  $\mathrm{Si}^{C_2H_5}_{Cl_3}$, and **ethyl silicic acid** (silico propionic acid), C_2H_5SiOOH, which is spontaneously inflammable, and forms salts with bases.

METALLO-ORGANIC COMPOUNDS.

The alcoholic or alkyl radicles form compounds by direct union with many of the metals, the most important of which are those with sodium, zinc, and mercury. Not only do they form saturated compounds, but many metals yield derivatives in which their atomicity is only in part satisfied by the alkyl groups, such a metallic group, if monad, forming a compound radicle which cannot be isolated, but which can combine with such groups as Cl or OH. The hydroxides thus produced are strongly basic, owing to the positive character of the alkyl groups.

We may conveniently study first a zinc alkyl.

Zinc Ethyl, $Zn(C_2H_5)_2$, *zinc ethide,* was first obtained by the action of zinc upon ethyl iodide. The reaction occurs in two stages: when heated to 90°—

$$2C_2H_5I + Zn_2 = 2C_2H_5ZnI$$

and this compound, heated to 160°, gives—

$$2C_2H_5ZnI = (C_2H_5)_2Zn + ZnI_2$$

This reaction, modified by working details, is usually employed for its production, use being made of zinc filings or the zinc-copper couple.

†*Process.*—Heat 36 grams of zinc filings in a dry flask with 4 grams of copper (prepared by reducing CuO in hydrogen at a low temperature) till the zinc becomes round and yellow, then shake strongly. When cool it should be a dark metallic powder.

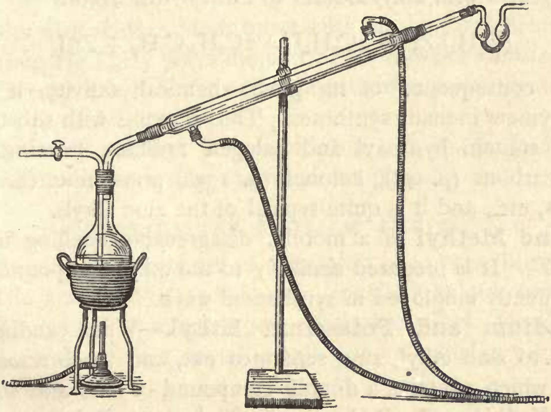


FIG. 43.

Connect the flask with a reflux condenser provided with a mercury trap, as Fig. 43.

Next pass perfectly dry CO_2 through the apparatus, and add 34·8 grams of ethyl iodide. Heat the whole to 90° till no more iodide distils back unchanged. Then cool the flask, and transfer it to the upper end of the condenser; distil the zinc ethyl off from an oil-bath at 160°, and collect in vessels full of CO_2 and separated by mercury traps from the air.

Caution.—Great care must be taken not to expose it to the air, because it is spontaneously inflammable.

Properties.—Zinc ethyl is a colourless, highly refractive, mobile liquid, with a peculiar odour, b.p. 118°, sp. gr. 1·182 at 18°. When exposed to air it ignites at once, and burns with a luminous green-tinged flame, clouds of zinc oxide being formed, and consequently it must be handled carefully in an atmosphere of carbon dioxide. When oxygen is allowed to act *slowly* on zinc ethyl, zinc-ethyl ethylate, $\begin{matrix}C_2H_5\\C_2H_5O\end{matrix}\!>\!Zn$, and then zinc ethylate, $(C_2H_5O)_2Zn$, are formed in succession. When added to water, zinc ethyl yields ethane and $Zn(OH)_2$; with alcohol, zinc ethylate and $Zn(OH)_2$. The halogens react violently on it, forming haloid esters.

It reacts with alkyl-iodides to form hydrocarbons—

$$(C_2H_5)_2Zn + 2C_2H_5I = 2C_2H_5.C_2H_5 + ZnI_2$$

In consequence of its great chemical activity, it finds employment in many syntheses. Thus it reacts with substances which contain hydroxyl and halogen radicles, forming, *e.g.*, hydrocarbons (p. 43), ketones (p. 135), phosphines (p. 172), arsines, etc., and it is quite typical of the zinc alkyls.

Zinc Methyl is a mobile, disagreeable-smelling liquid, b.p. 46°. It is prepared similarly to the ethyl compound, and is frequently employed in synthetical work.

Sodium and Potassium Ethyl.—When sodium is added to zinc ethyl, zinc separates out, and there remains a liquid which contains a double compound of zinc and sodium ethyl, $NaC_2H_5 + Zn(C_2H_5)_2$, from which the sodium compound has not yet been freed. Potassium acts similarly. These compounds are even more reactive than the zinc alkyls, and absorb CO_2, forming propionates—

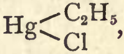
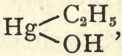
$$C_2H_5Na + CO_2 = C_2H_5COONa$$

while CO forms a ketone.

Mercury Ethyl, $Hg(C_2H_5)_2$, *mercury ethide*, was first prepared by decomposing mercuric chloride by zinc ethyl, but is best obtained by the action of sodium amalgam (0·2 per cent. Na) upon ethyl iodide in presence of acetic ether—

$$Hg + Na_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI$$

The excess of the reagents is distilled off, water added, and the separated oil dried over $CaCl_2$, and then rectified.

Properties.—Mercuric ethyl is a *very poisonous*, colourless, heavy liquid, with a faint ethereal odour, b.p. 159°, sp. gr. 2·46. It is not acted upon by water, in which it is insoluble, and does not ignite in air till heated, but takes fire in chlorine. Mercury ethyl yields **chlor-mercuric ethyl,**  $Hg\begin{array}{l}<C_2H_5\\<Cl\end{array}$, when treated with alcoholic mercuric chloride; and the chlor-ethide gives, with moist silver oxide, **hydroxy-mercuric ethyl,**  $Hg\begin{array}{l}<C_2H_5\\<OH\end{array}$, which is a strongly alkaline substance forming salts with acids. Many other salts can be formed, in which the group $Hg.C_2H_5'$ plays the part of a *compound radicle.*

Mercury ethyl finds employment in certain synthetical work.

Mercury methyl is a liquid, b.p. 95°, sp. gr. 3·069, and still more poisonous than the ethyl compound.

REMARKS ON THE METALLIC DERIVATIVES.

Three typical methods of formation have been illustrated: (1) The action of a metal upon an alkyl haloid (see Zinc ethyl); (2) of a metal upon a metallic alkyl (see Sodium ethyl); and (3) of a metallic salt upon a metallic alkyl (see Mercuric ethyl).

CHAPTER XXIV.

ACID AMIDES AND AMIDO-ACIDS.

ACID AMIDES.

HITHERTO the compounds of nitrogen which have been under consideration have contained the amidogen group linked to an alkyl radicle; that is, they have been derived from alcohols by the replacement of the hydroxyl group by NH_2.

We must now consider a class of compounds derived from acids in a similar manner, and hence known as acid amides. Thus C_2H_5OH yields $C_2H_5NH_2$, and $CH_3.COOH$ yields $CH_3.CONH_2$. These substances, unlike alkylamines, are neutral to litmus, although they are sufficiently basic in their properties to form compounds with acids.

The first of the series is that derived from formic acid, **Formamide,** $H.CONH_2$, which was first obtained by heating ethyl formate with ammonia in sealed tubes to 100° C., and is a colourless liquid, boiling at 192°–195°.

A better substance to study in detail is—

Acetamide, $CH_3.CONH_2$, which was first prepared (*1) by heating ethyl acetate to 120° with strong aqueous ammonia—

$$CH_3.CO.OC_2H_5 + NH_3 = CH_3.CONH_2 + C_2H_5OH$$

(*2) When ammonium acetate is distilled in a current of dry ammonia, or, more conveniently, heated in closed tubes to 230°, and then distilled, acetamide is produced—

$$CH_3.CO.ONH_4 = CH_3.CONH_2 + H_2O$$

†*Process.*—Heat 100 grams of ammonium acetate in well-sealed glass tubes for 6 hours to 230°. (The acetate may be prepared by passing dry NH_3 into glacial acetic acid till it is saturated.) At the end of that time carefully open the tube and distil the contents, collecting all above 180° separately. On standing, crystals of acetamide separate, which can be drained, and, on distillation, will yield nearly pure acetamide.

It is also formed (*3) when ammonia acts on acetyl chloride—

$$CH_3.COCl + 2NH_3 = CH_3.CONH_2 + NH_4Cl$$

This last method clearly indicates its constitution.

Properties.—Acetamide is a white, crystalline, deliquescent solid, sp. gr. 1·159, m.p. 83°, b.p. 222° (cor.), and it may be heated to nearly 360° without decomposition. It ordinarily possesses a strong smell of mice; if pure is probably odourless. It is soluble in water or alcohol, but insoluble in pure ether. If heated with water, acids, or with aqueous solutions of alkalis, acetamide is resolved into acetic acid and ammonia—

$$CH_3.CONH_2 + HOH = CH_3.COOH + NH_3$$

Nitrous acid also forms the free acid by a similar reaction to that which occurs when it acts on an amine (see p. 168)—

$$CH_3.CONH_2 + HONO = CH_3.COOH + N_2 + H_2O$$

When distilled with P_2O_5 or $ZnCl_2$ acetamide yields acetonitrile (see p. 193); while PCl_5 reacts with it, replacing the oxygen atom, and halogens replace one of the hydrogen atoms in the NH_2 group. It is a weak base, and combines directly with the stronger acids; thus gaseous HCl passed into a solution of it in alcohol-ether forms the compound $CH_3.CONH_2.HCl$. On the other hand, it is also slightly acid in character, and can form metallic compounds, of which C_2H_3ONHAg is an example.

GENERAL REMARKS ON THE ACID AMIDES.

Acid amides can be formed (1) by the action of NH_3 on esters, (2) by dehydration of the ammonium salts of acids, and (3) by acting on acid chlorides with NH_3. These methods have been illustrated by the formation of acetamide. It can also be produced (4) by the action of ammonia on acid anhydrides.

Properties.—The acid amides are generally solid crystalline substances soluble in alcohol and in ether; the lower members of the series are soluble in water. They act as feebly basic compounds, although neutral to litmus. The amide hydrogen is replaceable by metals, and also by acid groups, such as acetyl, C_2H_3O', and by the halogens. (For the reactions which they undergo with water, acids, alkalis, nitrous acid, P_2O_5, and PCl_5, see Acetamide.)

Constitution.—The constitution of these amides may be deduced from their formation by method 3, and the reactions they undergo with water, the alkalis, and nitrous acid.

AMIDO-ACIDS.

Glycocoll or **Glycine**, $CH_2NH_2.COOH$, *amido-acetic acid.*—This acid is the first representative of, and serves to illustrate, a series of substances which, though neutral in reaction, possess both acid and basic properties. It *may* be viewed as derived from an alcoholic acid, $CH_2OH.COOH$, by the replacement of the alcoholic OH by NH_2; but it is simpler to consider it as an amido-substitution derivative of the acid to which it is related: its formation by method (3) supports the latter view.

Glycocoll (γλυκύς, "sweet"; κόλλα, "glue") is obtained (1) as a decomposition product of glue when boiled with dilute H_2SO_4 or KOH; and (2) it is conveniently prepared from hippuric acid, which is found in the urine of horses, by boiling it with HCl or H_2SO_4—

$$\underset{\text{Hippuric acid}}{CH_2NH(C_6H_5CO).COOH} + H_2O = \underset{\text{Glycocoll}}{CH_2NH_2.COOH} + \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

Process.—Boil hippuric acid with four parts of strong HCl for an hour or two. Cool the solution, filter from benzoic acid, and separate the remainder of that substance by extraction with ether. Evaporate the residual liquid to the crystallising point, when glycocoll hydrochloride is obtained. If this is decomposed by either lead or silver oxide, the glycocoll is obtained free.

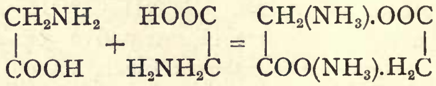
Glycocoll is *synthetically* produced (*3) by heating chloracetic acid with ammonia (compare Formation of amines)—

$$CH_2Cl.COOH + NH_3 = CH_2NH_2.COOH + HCl$$

and (4) by passing cyanogen into boiling concentrated solution of hydriodic acid—

$$CN.CN + 5HI + 2H_2O = CH_2NH_2.COOH + NH_4I + 2I_2$$

Properties.—Glycocoll crystallises in colourless monoclinic tablets, which melt with decomposition at 230°–236°. It is soluble in water, insoluble in absolute alcohol and in ether, and has a sweet taste. It contains the groups NH_2 and COOH, and can form compounds with both acids and bases; it is *neutral* to litmus, and is probably itself a salt formed by one molecule neutralising another, thus—



$$\begin{array}{c} CH_2NH_2 \\ | \\ COOH \end{array} + \begin{array}{r} HOOC \\ | \\ H_2NH_2C \end{array} = \begin{array}{lr} CH_2(NH_3).OOC & \\ | & | \\ COO(NH_3).H_2C & \end{array}$$

This formula is supported by the fact that it forms *two* compounds with hydrochloric acid. Nitrous acid converts it into glycollic acid (*q.v.*), and when heated with BaO it yields methylamine and $BaCO_3$. KOH acts similarly. Solutions of glycocoll give, with ferric chloride, a deep red colour, which acids discharge and ammonia restores.

Glycocoll prevents the precipitation of copper salts by KOH. Its metallic salts are probably formed by metals replacing hydrogen in the amidogen group.

Alanine, *amido-propionic acid*, and the amido-butyric acids, do not call for any special remark; but—

Leucine, $CH_3.(CH_2)_3.CH(NH_2).COOH$, or *α-amido-caproic acid*, found in many animal juices, may be mentioned. It occurs in the liver during disease, and in the brain and the pancreas; also in old cheese, and is found during the decay of albumenoids. It crystallises in leaflets, m.p. 170°. It is slightly soluble in water, insoluble in ether, and lævo-rotatory in its action on polarised light.

SECTION III.

CYANOGEN AND CARBONIC ACID DERIVATIVES.

CHAPTER XXV.

CYANOGEN AND ITS DERIVATIVES.

Cyanogen is the name given to the compound radicle (CN), which, however, does not exist in the free condition, but only as the gas cyanogen, better termed di-cyanogen, CN.CN. This *may* be looked upon as a derivative of a hydrocarbon, but it is not usual to do so.

It is convenient, therefore, to study the compounds apart, and it will be noticed that the CN group combines with metallic and organic radicles in a manner somewhat analogous to that in which the halogens combine. In fact, the student will remember many reactions already mentioned in which it has displaced one of those elements. The group CN is often written Cy.

Syntheses of Cyanogen Derivatives.

The following synthetical processes are especially interesting in illustrating the combination of carbon with nitrogen.

1. Carbon and nitrogen do not combine together very readily alone, although cyanogen is formed when electric sparks are passed between carbon poles in an atmosphere of nitrogen—

$$C_2 + N_2 = C_2N_2$$

2. Although the combination between the two elements occurs so difficultly alone, if nitrogen is passed over a heated

mixture of potassium carbonate, or barium oxide, and carbon, cyanide of potassium or barium is formed—

$$4C + N_2 + K_2CO_3 = 2KCN + 3CO$$
$$3C + N_2 + BaO = Ba(CN)_2 + CO$$

The production on a large scale of potassium ferrocyanide by heating nitrogenous organic matter with alkalis and iron is an analogous case.

3. Also if ammonia is passed over red-hot charcoal, ammonium cyanide is produced—

$$C + 2NH_3 = (NH_4)CN + H_2$$

4. Again, cyanogen itself is produced when ammonia and coal-gas are burned together in a Bunsen burner—

$$2CO + 2NH_3 + O = C_2N_2 + 3H_2O$$

These examples will suffice to illustrate the synthetical formation of cyanogen compounds from inorganic sources, and the following bodies or classes of compounds will now be studied in order :—

Cyanogen or di-cyanogen, CN.CN.

Hydrocyanic acid, HCN.

Metallic cyanides; *e.g.* potassium cyanide, potassium ferrocyanide.

Esters of hydrocyanic acid; *e.g.* CH_3CN.

Cyanic acid and cyanates, HOCN.

Cyanogen chloride, Cl.CN.

Cyanuric acid and cyanurates, $H_3O_3(CN)_3$.

Cyanogen (*κύανος*, "blue"), CN.CN, is usually obtained (1) by the decomposition of cyanides. Thus, on heating mercuric cyanide it is formed along with the polymeric black solid **paracyanogen**—

$$Hg(CN)_2 = C_2N_2 + Hg$$

It may also be conveniently obtained from copper cyanide as described below.

Process.—Heat a concentrated aqueous solution of KCN with 2 parts $CuSO_4.5H_2O$, dissolved in 4 parts of water, and collect the gas over mercury. *Remember the gas is very poisonous.*

(2) Cyanogen is a product of the combustion of ammonia

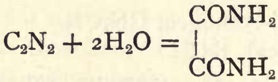
with coal-gas (p. 187), and occurs in the gases from coke ovens.

(3) Of special synthetic importance is its formation from its elements by the action of electricity (p. 186); and (4) also its production when ammonium oxalate or oxamide is heated with dehydrating agents, *e.g.* P_2O_5—

$$\underset{\text{Ammonium oxalate}}{C_2O_4(NH_4)_2} = C_2N_2 + 4H_2O$$

Properties.—Cyanogen is a colourless gas with a peculiar odour, and is *very* poisonous. It burns with a violet flame; cold and pressure condense it to a liquid, b.p. −20·7°, and a lower temperature produces a solid, m.p. −34·4°. It is slightly soluble in water, more so in alcohol.

Aqueous solutions decompose on standing, with the production of brown *azulmic acid*, ammonium oxalate, and other bodies. Potash forms the cyanide and the cyanate, but if a little aldehyde is present in the aqueous solution, oxamide only is formed—



$$C_2N_2 + 2H_2O = \begin{array}{l} CONH_2 \\ | \\ CONH_2 \end{array}$$

These reactions, coupled with its formation from ammonium oxalate, show it to be the nitrile of oxalic acid.

HYDROCYANIC ACID AND THE CYANIDES.

Hydrocyanic Acid, HCN, *prussic acid,* occurs in tobacco smoke, and is found in many plants; *e.g.* it is present in bitter almonds, cherry-stones, etc. These bodies contain a substance called amygdalin, which is decomposed if they are macerated in water, and on distillation hydrocyanic acid is found in the distillate.

It is obtained synthetically (1) by the direct union of cyanogen and hydrogen induced by the silent electric discharge—

$$H_2 + C_2N_2 = 2HCN$$

also (2) when electric sparks are passed through a mixture of acetylene and nitrogen—

$$C_2H_2 + N_2 = 2HCN$$

and (3) by rapidly heating ammonium formate with P_2O_5—

$$H.COONH_4 = HCN + 2H_2O$$

In the last reaction it appears as the nitrile of formic acid.

It is usually obtained by decomposing cyanides by acids (for synthetical formation of cyanides, see p. 186), and as it is exceedingly poisonous great care must be exercised in its preparation—

$$\underset{\text{Potassium ferrocyanide}}{2K_4FeC_6N_6} + 3H_2SO_4 = 3K_2SO_4 + Fe_2K_2C_6N_6 + 6HCN$$

$$KCN + \underset{\text{Tartaric acid}}{C_4H_6O_6} = HCN + KHC_4H_4O_6$$

Processes.—Distil a mixture of 14 parts water, 7 parts conc. H_2SO_4, and 10 parts coarsely powdered potassium ferrocyanide in a capacious flask connected with a condenser and receiver, and collect the gas in distilled water. If required anhydrous, the gas is passed through an inverted condenser, dried over calcium chloride (both the condenser and vessels containing $CaCl_2$ being kept at 30°), and collected in a receiver surrounded by ice and salt. To obtain an acid of known strength, shake together 9 parts tartaric acid, 60 parts water, and 4 parts KCN. Allow the acid tartrate of potassium to separate, and pour off the liquid, which then contains 3·6 per cent. of HCN.

Properties.—Pure hydrocyanic acid is a colourless, mobile liquid, b.p. 26·5°, sp. gr. 0·7058 at 7°. It has a peculiar smell resembling that of oil of bitter almonds. It is **intensely** poisonous; one drop of the anhydrous acid is an instantly fatal dose, and minute quantities of the vapour are sufficient to kill when inhaled. The acid is readily inflammable; it is unstable, especially in aqueous solutions, but a trace of a mineral acid renders it more stable. When heated with concentrated mineral acids, or with alkalis it yields formic acid and ammonia (compare Cyanogen)—

$$HCN + 2H_2O = H.COOH + NH_3$$

It is reduced by nascent hydrogen to methylamine. It is only a *very* feeble acid, but yields a series of salts with the metals, acting like a haloid acid, and gives a white precipitate with silver salts.

Identification.—Hydrocyanic acid gives a blue colour, due to prussian blue, when the solution is first made alkaline with NaOH, then a solution of $FeSO_4$ and $FeCl_3$ added, and finally HCl. The following is a more delicate test: add a few drops of yellow ammonium sulphide to the liquid containing the acid, evaporate to dryness, add a few drops of water and a drop of solution of $FeCl_3$; a deep red colour, due to ferric thiocyanate, is produced.

Constitution.—It is possible to write the constitutional formula of hydrocyanic acid in two ways, viz. H.C:N and as HN⋮C; which of these formulæ is correct cannot be determined, though probably the former is nearer the truth. One of the cyanides, however, silver cyanide, appears to be differently constituted from the others, as in certain reactions it behaves as if it were best represented by the formula Ag.NC, in which the silver is united to the nitrogen; but there are no *series* of salts corresponding to the two forms of acid.

The alkyl derivatives or esters, however, show marked differences: there are two series of them, apparently derived from HCN and HNC respectively. Those derived from HCN are termed **cyanides** or **nitriles,** while the others are called **iso-cyanides** or **carbamines.**

Simple Cyanides.—The cyanides of the alkalis and alkaline earths are readily soluble in water. Cyanides of the other metals, mercuric cyanide excepted, are insoluble; many of them, however, dissolve in solutions of alkaline cyanides, forming soluble double cyanides.

The principal cyanides are mentioned below.

Potassium Cyanide, KCN, is found in blast furnaces, and its production from K_2CO_3, nitrogen, and carbon has been mentioned (p. 187). It is also formed when potassium is heated in cyanogen.

When required quite pure, potassium cyanide is prepared by passing anhydrous HCN into strong KOH, when it is precipitated, and can be collected, washed with alcohol, and dried. It is usually formed by heating potassium ferrocyanide with K_2CO_3 in a crucible—

$$2K_4Fe(CN)_6 + 2K_2CO_3 = 10KCN + 2KCNO + 2Fe + 2CO_2$$

So prepared, as indicated by the equation, it always contains cyanate. It can also be prepared in an almost pure state by igniting potassium ferrocyanide alone, and filtering the melted product through hot porous crucibles, so as to separate the carbide of iron—

$$K_4FeCy_6 = 4KCN + N_2 + FeC_2$$

Potassium cyanide is a white deliquescent solid, which crystallises in cubes and fuses at a red heat. It is very soluble in water, and is readily decomposed by acids, even by CO_2. It is *very* poisonous, is a powerful reducing agent, being readily oxidised to potassium cyanate, and forms double cyanides with other metals.

Silver Cyanide, $AgCN$, is prepared as a white curdy solid by adding potassium cyanide to solutions of silver salts. It may be dried at 100°, and does not blacken on exposure to light, is little soluble in HNO_3, but readily in KCN, forming $AgCN.KCN$, also in NH_4HO (compare $AgCl$).

Mercuric Cyanide, $Hg(CN)_2$, is prepared by boiling Prussian blue with HgO and water, or by dissolving HgO in the acid. It is readily soluble in water, but not in absolute alcohol. Is decomposed on heating, yielding cyanogen. It forms many double compounds with cyanides and other salts.

Compound Cyanides.—Many of the insoluble cyanides form, with those of the alkali and other metals, soluble double cyanides. Those with the alkali metals are decomposed by mineral acids, with precipitation of the insoluble cyanides and liberation of HCN.

Some of the cyanides, however, appear to enter into more intimate combination, so that on acidification a new acid is liberated, and not HCN. Of this class the ferrocyanides and ferricyanides are noteworthy examples.

Potassium Ferrocyanide, $K_4FeCy_6.3H_2O$, *yellow prussiate of potash.*—It is well known that when nitrogenous organic matter is fused with potashes, KCN is formed. It is practically impossible to purify this complex product so as to obtain the cyanide direct; but if along with this mixture iron is introduced, on lixiviating the fused mass crystals of potassium ferrocyanide separate and can be recrystallised. The reaction which occurs is complex, but it may perhaps be represented thus—

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$

or, as potassium thiocyanate is always formed, thus—

$$13KCN + Fe_2S_3 = 2K_4Fe(CN)_6 + 2K_2S + KSCN$$

The sulphur comes both from the organic matter, and from the reduction of K_2SO_4 present in the carbonate.

Manufacture.—The above reaction is realised by heating, on the iron hearth of a reverbatory furnace, iron and K_2CO_3, and when fusion has occurred, introducing animal matter, *e.g.* horn, blood, wool, or leather, along with more K_2CO_3. When the fusion is complete, the melt is ladled out and cooled. The "metal" is then extracted with water, and the solution allowed to crystallise.

Properties.—Potassium ferrocyanide forms lemon-coloured quadratic pyramids which lose their water at 60°–80°. It has a sweet saline taste, and is not poisonous. Its solution decomposes when exposed to sunlight, liberating HCN and precipitating "Prussian blue." When ignited it yields KCy, carbide of iron, and nitrogen, and when heated with conc. H_2SO_4, gives carbon monoxide—

$$K_4Fe(CN)_6 + 6H_2O + 6H_2SO_4 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4$$

When a solution of potassium ferrocyanide is poured into excess of ferric chloride, a blue precipitate is formed called **Prussian blue**, which is ferric ferrocyanide—

$$4FeCl_3 + 3K_4(FeCy_6) = Fe_4(FeCy_6)_3 + 12KCl$$

When washed and dried this forms a dark blue amorphous powder, insoluble in water, soluble in oxalic acid.

Potassium Ferricyanide, K_3FeCy_6 *red prussiate of potash*, is formed when the ferrocyanide is treated with oxidising agents, *e.g.* chlorine or PbO_2—

$$2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl$$

The chlorine is well washed and passed in till the solution no longer yields a blue colour with ferric salts. Excess of the gas must be avoided, or Prussian green is precipitated.

Properties.—It forms large red crystals, soluble in water and nearly insoluble in alcohol. It is used as an oxidising agent, especially in alkaline solutions, becoming reduced to ferrocyanide, and finds employment in quantitative analysis on that account. When a solution of potassium ferricyanide is added to excess of a ferrous solution, a blue precipitate is obtained of ferrous ferricyanide, or **Turnbull's blue,** $Fe_3(FeCy)_2$. When dry it is a deep blue powder, insoluble in water and alcohol, and soluble in oxalic acid.

ESTERS OF HYDROCYANIC ACID, OR NITRILES.

Hydrogen cyanide or formo-nitrile, $H.CN$
Methyl ,, ,, aceto-nitrile, $CH_3.CN$
Ethyl ,, ,, propio-nitrile, $C_2H_5.CN$, etc.

It has been already pointed out that, by its formation from ammonium formate (p. 189) and decomposition with dilute alkalis (p. 189), hydrocyanic acid appears to be the nitrile of formic acid.

It will be sufficient to study in detail the methods of formation and typical reactions of the second member of the series.

Methyl Cyanide, or **Aceto-nitrile,** $CH_3.CN$, occurs in crude benzene and in the distillation products of beet-root vinasse, and can be produced in a number of ways. Thus (*1) making use of a method indicated (p. 119) for the formation of esters, if methyl potassium sulphate is distilled with dry potassium cyanide, aceto-nitrile is formed—

$$CH_3SO_4K + KCN = CH_3.CN + K_2SO_4$$

A small amount of the iso-cyanide is also formed, which can be got rid of by shaking with dilute HCl, neutralising with soda, and drying over fused $CaCl_2$. (*2) Another useful way is to distil acetamide, or dry ammonium acetate, with P_2O_5, which acts as a dehydrating agent—

$$CH_3.CONH_2 - H_2O = CH_3.CN$$
$$CH_3.COONH_4 - 2H_2O = CH_3.CN$$

And finally, (*3) it has recently been shown that thionyl chloride decomposes acetamide, with production of the nitrile, the yield being very good—

$$CH_3.CONH_2 + SOCl_2 = CH_3.CN + 2HCl + SO_2$$

The reactions with P_2O_5 or $SOCl_2$ may be used to prepare it.

Properties.—Aceto-nitrile is a colourless liquid, b.p. 81.6°, sp. gr. 0·805 at $\underline{0}^{\circ}$. It has a pleasant odour, is miscible with water and alcohol, and thrown out of its solution in the former by salts.

The two following reactions which it undergoes are typical of the nitriles: (1) if boiled with alkalis or acids, it yields acetic acid and ammonia—

$$CH_3.CN + KOH + H_2O = CH_3.COOK + NH_3$$
$$CH_3.CN + HCl + 2H_2O = CH_3.COOH + NH_4Cl$$

and (2) on reduction with nascent hydrogen (sodium and alcohol), it yields ethylamine—

$$CH_3.CN + 2H_2 = CH_3.CH_2NH_2$$

In connection with the former reaction, it should be specially noted that not only is it an exceedingly general way of producing acids, but it is also an important link in a series of reactions which enable us to prepare homologous compounds from those which contain a carbon atom less. Thus the following series may be mentioned, each member of which can be prepared from that which immediately precedes it by reactions already indicated :—

C_2H_5OH	C_2H_5I	C_2H_5CN	C_2H_5COOH	$C_2H_5CH_2OH$
Ethyl alcohol	Ethyl iodide	Ethyl cyanide	Propionic acid	Propyl alcohol

ISOCYANIDES, ISO-NITRILES, OR CARBAMINES.

The properties of these bodies, which are isomeric with the nitriles, may be illustrated by **methyl isocyanide,** $CH_3.NC$, or *methyl carbamine.* It is formed (*1) when methyl iodide, diluted with ether, is heated with two molecules of AgNC for several hours in a closed tube to 130°. The crystalline compound $AgNC + CH_3.NC$ is first formed, and is then distilled with water and KCN—

$$CH_3I + AgNC = CH_3.NC + AgI$$

(*2) It is also very characteristically formed when methylamine is heated with alcoholic KOH and chloroform—

$$CH_3NH_2 + CHCl_3 + 3KOH = CH_3.NC + 3KCl + 3H_2O$$

also from alkyl sulphates and KCN (see Nitriles).

Properties.—Methyl carbamine is a colourless, stinking liquid, b.p. 59·6°, sp. gr. 0·756 at 4°. Its vapour produces nausea and headache. Unlike aceto-nitrile, it is not acted upon by alkalis; but acids resolve it into formic acid and methylamine—

$$CH_3.NC + 2H_2O = CH_3NH_2 + HCOOH$$

Water at 180° produces the same reaction. HgO oxidises it to methyl isocyanate.

Constitution of Nitriles and Isonitriles.—The different manner in which the two classes of substances react with dilute acids clearly brings out the difference between them. Thus the nitrile loses its nitrogen atom easily in the form of ammonia, the carbon of the CN group remaining fixed, while on reduction an amine is produced—hence the carbon is apparently the linking atom of the CN group; on the contrary, the isonitriles readily lose carbon with production of formic acid and an amine. These facts lead to the formulæ $CH_3—C\equiv N$ and $CH_3—N\equiv C$ in the two cases.

Oxygen Compounds of Cyanogen; Cyanic and Cyanuric Acids.

Cyanic Acid, HOCN, cannot be obtained from its salts by the action of acids, but only by heating its polymer cyanuric acid in a current of CO_2, and condensing the vapours in a receiver surrounded by a freezing mixture. Some of the polymeric substance **cyamelide** is always formed.

Properties.—Cyanic acid is a mobile, volatile liquid, sp. gr. 1·14 at 0°. It is strongly acid, smells like glacial acetic acid, and its aqueous solutions break up at about 0°, according to the following equation:—

$$HOCN + H_2O = CO_2 + NH_3$$

It changes quickly into the white polymeric solid cyamelide at 0°; above that temperature the reaction is very violent.

Constitution.—There are two possible structural formulæ for this acid—

$N{\equiv}C{-}OH$	$O{=}C{=}NH$
Normal cyanic acid	Isocyanic acid

It is not known, however, which is the correct one; but though there is no known distinction between the two possible acids, and there are not two series of metallic salts corresponding to them, there are two series of esters.

Cyanates.—The salts are probably derivatives of the iso-acid. Two of them only will be noted.

Potassium Isocyanate, $CO{:}NK$, *ordinary cyanate of potassium*, is readily formed by the oxidation of potassium cyanide by heating in the air or in the presence of an easily reducible oxide—

$$KCN + PbO = CO{:}NK + Pb$$

It is usually formed by heating ferrocyanide of potassium with some oxidising agent, *e.g.* $K_2Cr_2O_7$, and extracting it with alcohol (see Urea, p. 202). The salt crystallises in colourless laminæ, which resemble $KClO_3$; it is readily soluble in water, but insoluble in absolute alcohol. Heat does not decompose it, but in presence of water it forms NH_3 and K_2CO_3.

Ammonium Isocyanate, $CO{:}N.NH_4$, is formed by mixing dry ammonia vapour with that of cyanic acid. Its solution on evaporation undergoes intramolecular change, with the formation of **urea** (see p. 202)—

$$CO{:}N.NH_4 = CO{:}(NH_2)_2$$

Cyanogen Chloride, $CNCl$, may be looked upon as the acid chloride of cyanic acid, and is formed when mercuric cyanide, $Hg(CN)_2$, is decomposed by chlorine. It is a colourless gas with pungent odour, which is condensible at $-15°$ to a liquid. It polymerises spontaneously, forming solid cyanuric chloride, $C_3N_3Cl_3$.

Cyanamide, $CN.NH_2$, is formed from the latter body by the action of ammonia; also by the action of HgO upon thiourea—

$$CS(NH_2)_2 + HgO = CN.NH_2 + HgS + H_2O$$

It is a white crystalline solid, m.p. 40°, which polymerises on heating.

Cyanuric Acid, $C_3N_3O_3H_3.2H_2O$, is a polymer of cyanic acid, and can be obtained (1) by boiling cyanuric chloride with dilute alkalis—

$$C_3N_3Cl_3 + 3H_2O = C_3N_3O_3H_3 + 3HCl$$

or (2) by leading dry chlorine into melted urea at 130°, dissolving out NH_4Cl by cold water, and recrystallising the acid—

$$3CON_2H_4 + 3Cl = C_3O_3N_3H_3 + 2NH_4Cl + HCl + N$$

Cyanuric acid crystallises (from water) with 2 molecules of water in rhombic prisms, which are efflorescent and soluble in water and alcohol. On distillation it yields cyanic acid (p. 195). There are two possible structural formulæ for it, and it yields *two* series of esters. Ordinary cyanuric acid is probably the normal acid, $(CN)_3(OH)_3$.

ESTERS OF CYANIC AND ISOCYANIC ACIDS.

Ethyl Cyanate, $CN.OC_2H_5$, *cyanetholine*, is said to be formed when cyanogen chloride is acted upon by sodium ethylate—

$$CNCl + C_2H_5ONa = CN.OC_2H_5 + NaCl$$

It is a colourless liquid, insoluble in water, and decomposes on distillation.

Ethyl Isocyanate, $CO:NC_2H_5$, *ethyl carbimide*, is an example of the ordinary cyanic esters. It may be obtained (*1) by distilling potassium ethyl sulphate with the ordinary cyanate of potassium (isocyanate) at 180°–250°—

$$CO:NK + C_2H_5SO_4K = CO:NC_2H_5 + K_2SO$$

and (*2) by the action of ethyl iodide upon silver cyanate (isocyanate)—

$$CO:NAg + C_2H_5I = CO:NC_2H_5 + AgI$$

It is a mobile liquid, b.p. 60°, sp. gr. 0·898, with a suffocating, penetrating smell. When heated with alkalis or aqueous acids it forms ethylamine, which shows that the nitrogen atom is directly united to the ethyl group—

$$CO{:}NC_2H_5 + 2KOH = C_2H_5NH_2 + K_2CO_3$$
$$CO{:}NC_2H_5 + H_2O + HCl = C_2H_5NH_2.HCl + CO_2$$

Thiocyanic Acids.

Just as there are apparently two possible cyanic acids, so there are two possible thiocyanic acids—

$N{\equiv}C{-}SH$	$S{=}C{=}NH$
Normal thiocyanic acid or sulphocyanic acid	Iso-thiocyanic acid or thiocarbimide

The normal acid is known, and the metallic thiocyanates are also normal (difference from cyanates). Esters of both the acids are also known.

Thiocyanic Acid, NC.SH, can be prepared by distilling its potassium salt with dilute H_2SO_4 (compare cyanic acid), or by decomposing the mercury salt with H_2S or HCl. It is a colourless liquid with a strong smell, which crystallises at 12·5°. It is soluble both in water and alcohol, and is a very strong acid, nearly equal in avidity to HCl. The anhydrous acid polymerises on standing; the aqueous acid is stable. Heat breaks it up into HCN and persulpho-cyanogen, $H_2C_2N_2S_3$. Ferric salts colour solutions of both the acid and its salts a deep red, hence its employment in inorganic analysis.

Potassium Thiocyanate, CN.SK, can be obtained by dissolving sulphur in an aqueous solution of KCN, but is usually prepared from potassium ferro-cyanide by fusion with K_2CO_3 and sulphur.

†*Process.*—Heat 64 grams of sulphur and 34 grams K_2CO_3 in a pot till they melt; then add 92 grams dry K_4FeCy_6 and heat till that salt is quite decomposed. Then extract with water, neutralise with H_2SO_4, evaporate to dryness, next extract with alcohol and recrystallise.

The salt is obtained as long white deliquescent crystals, which resemble KNO_3.

Ammonium Thiocyanate is obtained by heating 8 parts carbon bisulphide with 30 parts ammonia in 30 parts alcohol, and concentrating to crystallisation—

$$CS_2 + 4NH_3 = CN.SNH_4 + (NH_4)_2S$$

It forms large white deliquescent plates, very soluble in water and alcohol. It melts at 147°, and if heated to about that temperature undergoes intra-molecular change with production of thio-urea (compare Ammonium cyanate).

Mercury Thiocyanate is formed when mercuric nitrate is added to a solution of potassium or ammonium thiocyanate. When burned it swells up (Pharaoh's serpents).

ESTERS OF THE THIOCYANIC ACIDS.

Esters of the Normal Acid may be formed from its potassium or silver salt and a haloid paraffin; *e.g.* (C_2H_5I)—

$$CN.SK + C_2H_5I = CN.SC_2H_5 + KI$$

and in other ways. They are liquids insoluble in water, with an odour like mercaptans. On reduction they yield mercaptans and HCN—

$$CN.SC_2H_5 + H_2 = C_2H_5SH + HCN$$

and oxidation produces sulphonic acids. Both these reactions show that the sulphur atom is united to the ethyl group.

Mustard Oils or **Isothiocyanic Esters**, *thiocarbimides*, are formed by a complex reaction from primary amines by the successive action of CS_2, and $HgCl_2$ or $AgNO_3$, and heating the product. This is what is termed Hofmann's "mustard oil test" for amines.

The mustard oils are all pungent-smelling liquids, which boil at a lower temperature than their isomers. Nascent hydrogen (Zn and HCl) reduces them to amines and thio-formaldehyde (compare Normal esters)—

$$CS:NC_2H_5 + 2H_2 = C_2H_5NH_2 + H.CHS$$

when heated with HCl to 100° they break up according to the equation—

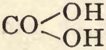
$$CS:NC_2H_5 + 2H_2O = C_2H_5NH_2 + CO_2 + H_2S$$

The liberation of amines in these and other reactions leads to the conclusion that in the mustard oils the nitrogen atom is the linking atom.

Allyl mustard oil will be described, p. 209.

CHAPTER XXVI.

DERIVATIVES OF CARBONIC ACID. UREA; URIC ACID.

THE hypothetical carbonic acid,  $CO<^{OH}_{OH}$ might be looked upon as the first of the series of hydroxy-acids (p. 224), but that the fact of its hydroxyl groups being both attached to the same carbonyl group, and being therefore of exactly equal value, gives it properties different from those of the other hydroxy-acids, in which the hydroxyl groups possess distinctly different values.

We need not discuss free carbonic acid, and its anhydride **carbon dioxide** is well known to the student of inorganic chemistry; but several of the derivatives of the acid will be mentioned.

Carbon Monoxide, CO, may be looked upon as the anhydride of formic acid, and is noticeable as being a free oxygenated carbon radicle. Its formation from formates (p. 139) and from $K_4FeC_6N_6$ (p. 192) has been noted, and it is useful in the synthesis of carbon acids (see pp. 143, 149) and in the formation of carbonyl chloride. At a red heat it is a powerful reducing agent.

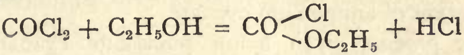
Carbonyl Chloride, $COCl_2$, *phosgene gas*, *carbon oxychloride*, is produced (1) by the direct union of carbon monoxide and chlorine in sunlight. It is also formed (2) when CO is lead into boiling antimony pentachloride, and (3) when chloroform is oxidised bv potassium dichromate and sulphuric acid. The first method, or a modification of it, is the best.

Phosgene gas is a colourless gas which condenses to a liquid, b.p. 8°. It acts as an acid chloride; thus it decomposes water—

$$COCl_2 + H_2O = CO_2 + 2HCl$$

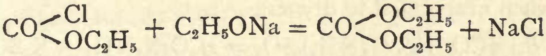
and also reacts with alcohols and ammonia (see below).

Esters of Carbonic Acid.—Phosgene gas acts upon alcohols, forming esters of **chlor-carbonic acid**, better named **chlorformic acid**; thus with C_2H_5OH it yields **ethyl chlor-carbonate**—



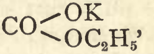
$$COCl_2 + C_2H_5OH = CO{<}^{Cl}_{OC_2H_5} + HCl$$

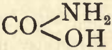
which gives **ethyl carbonate** by treatment with sodium ethylate—

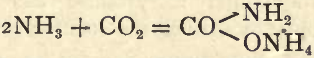


$$CO{<}^{Cl}_{OC_2H_5} + C_2H_5ONa = CO{<}^{OC_2H_5}_{OC_2H_5} + NaCl$$

This body is also formed when ethyl iodide acts on silver carbonate. These esters are ethereal smelling liquids.

The acid esters cannot exist free, but **potassium ethyl carbonate,**  $CO{<}^{OK}_{OC_2H_5}$, is produced when CO_2 is passed into an alcoholic solution of KOH in absolute alcohol, and is a white solid which forms pearly scales. It is readily saponified by water.

Carbamic Acid,  $CO{<}^{NH_2}_{OH}$, *amido-formic acid,* is not known in a free state, but its ammonium salt is obtained by the action of ammonia upon carbon dioxide—



$$2NH_3 + CO_2 = CO{<}^{NH_2}_{ONH_4}$$

This body absorbs water, and yields ammonium carbonate.

The ethereal salts, known as *urethanes*, are obtained by acting with ammonia upon chlorformic esters or the esters of carbonic acid.

Urea, $CO(NH_2)_2$, **carbamide,** the amide of carbonic acid, is an important product of vital action, and is contained in considerable quantity in human urine and in that of all mammals, especially those which are carnivorous, as well as in other animal juices. Its synthesis by Wöhler, in 1828, from ammonium cyanate, marks an epoch in the history of chemical theory. It can be prepared from urine as follows:—

Process.—Evaporate urine to a syrup, and add pure HNO_3. Nitrate of urea separates; recrystallise this from dilute HNO_3, and decompose it by K_2CO_3. The urea is separated from the KNO_3 formed by extraction with alcohol, and allowed to crystallise from that solvent.

Urea is synthetically obtained (1) by the intra-molecular transformation of ammonium cyanate.

In the process given below potassium cyanate is first formed (p. 196); this salt is decomposed by ammonium sulphate, and the solution of ammonium cyanate thus produced gives urea when evaporated to dryness—

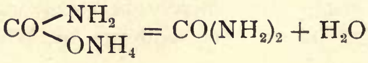
$$\text{(i.)}\quad 2CO{:}NK + (NH_4)_2SO_4 = 2CO{:}N.NH_4 + K_2SO_4$$
$$\text{(ii.)}\quad CO{:}N.NH_4 = CO(NH_2)_2$$

†*Process.*—Intimately mix 120 grams of well-dried anhydrous ferrocyanide of potash with 45 grams of dry potassium carbonate, and heat in a covered iron crucible till it just melts; lift out, cool a little, and add little by little, with stirring, 225 grams of red lead. Put the crucible in the fire again, and keep the mixture melted for a little time; then allow the lead to settle; pour off the melt on to an iron plate, and allow to cool (potassium cyanate could be extracted by alcohol from this if desired). Break up the solid, dissolve in 230–250 c.c. water, and add a concentrated solution of 120 grams *neutral* sulphate of ammonium. Evaporate the liquid to smaller bulk; potassium sulphate crystallises out. Separate the liquid, and evaporate it to dryness. Extract the residue with alcohol, and recrystallise the urea obtained, if necessary purifying it by shaking the solution with animal charcoal.

Urea is also synthetically formed (2), as might be expected, when either carbonyl chloride or ethyl carbonate is treated with ammonia (compare Acetamide, p. 182)—

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$$
$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2C_2H_5OH$$

and (3) also when ammonium carbonate (carbamate) is heated—



$$CO{<}^{NH_2}_{ONH_4} = CO(NH_2)_2 + H_2O$$

Properties.—Urea crystallises in long colourless needles or prisms, m.p. 132°, sp. gr. 1·323, and has a taste resembling saltpetre. It is soluble in water and alcohol. When heated above its melting point it decomposes into biuret, cyanuric acid, etc. Heated with water above 100° in closed tubes or with solutions of alkalis or acids, it is decomposed thus—

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$

Hypochlorites and hypobromites decompose urea with liberation of nitrogen and carbon dioxide, and this liberation of nitrogen is used as a test for the quantity present in urine—

$$CO(NH_2)_2 + 3NaOCl = CO_2 + N_2 + 3NaCl + 2H_2O$$

Nitrous acid acts similarly—

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O$$

Like acetamide, it combines with acids, the nitrate being the most characteristic salt, and it also forms a characteristic precipitate with $Hg(NO_3)_2$.

Constitution.—Urea must be looked upon as the amide of carbonic acid, since it is formed from ethyl carbonate and carbonyl chloride by reactions which are quite analogous to those which yield acetamide.

Identification.—In the presence of ammonium salts urea is often difficult to identify; the following tests assist in detecting it: It yields NH_3 when heated alone or with alkalis, and gives off nitrogen with hypochlorites. When heated to 150° it forms biuret; if this is dissolved in water, a few drops of $CuSO_4$ solution added, and then NaOH solution, a red to violet colour is obtained.

There are many sulphur compounds which are analogous to the oxides of carbon and the carbonates.

Carbon Monosulphide, CS, is obtained as a red powder by the action of light on the disulphide.

Carbon Oxy-sulphide, COS, *carbonyl sulphide*, is produced (1) when sulphur vapour and CO are passed through red-hot tubes; and (2) potassium thiocyanate is heated with H_2SO_4 diluted with an equal volume of water—

$$KCNS + 2H_2SO_4 + H_2O = COS + KHSO_4 + NH_4HSO_4$$

It is a heavy colourless gas with a slightly aromatic odour, and is decomposed by alkalis and alkaline earths, forming carbonates and sulphides.

Tri-thio-carbonic Acid, $CS(SH)_2$.—When alcohol and ether are added to a solution of Na_2S, which contains CS_2, sodium tri-thio-carbonate separates out; this salt yields the free acid as a brown oily liquid when it is decomposed by HCl. Ethereal salts of it are known.

Carbon Disulphide, CS_2, may be looked upon as the sulphanhydride of tri-thio-carbonic acid. It is produced by passing sulphur vapour over ignited carbon. It is a colourless, highly refractive liquid, b.p. 46°, sp. gr. 1·292 at $\frac{0^\circ}{4^\circ}$. If thoroughly purified it has an ethereal odour, but as usually obtained its odour is very disagreeable. Its vapour is very poisonous. It is almost insoluble in water, and is a useful solvent for oils, fats, and resins. Its analogy to CO_2 is shown by its union with metallic sulphides to produce tri-thio-carbonates.

Thio-carbonyl Chloride, $CSCl_2$, may be obtained by the action of chlorine, or of PCl_5, upon CS_2—

$$CS_2 + PCl_5 = CSCl_2 + PCl_3S$$

It is a red liquid, b.p. 70°, with a pungent odour resembling that of $COCl_2$.

Thio-urea, $CS(NH_2)_2$, or *sulpho-carbamide*, is obtained when ammonium thiocyanate is heated to 170°–180° for several hours (compare the formation of urea from ammonium cyanate, p. 202). When perfectly pure it crystallises in rhombic prisms, m.p. 169°. It decomposes on heating with alkalis or acids—

$$CS(NH_2)_2 + 2H_2O = CO_2 + 2NH_3 + H_2S$$

(compare Urea), and it forms a crystalline nitrate.

Uric Acid, $C_5H_4N_4O_3$, *lithic acid*, is found in many animal substances, either free or as a salt. Thus it is found free (and as the ammonium salt) in the urine of both carnivorous and herbivorous animals, especially of the former; also in human urine. Serpents' excrement consists almost entirely of ammonium urate, and it is largely present in guano. In gout it is found in the blood as the acid sodium salt. The acid can be prepared artificially, amongst other methods, by heating urea and glycocoll together.

Preparation.—Uric acid is best prepared by dissolving out oxalates, phosphates, and carbonates from guano by treatment with dilute HCl, boiling the residue with caustic soda, and acidifying the clear solution with HCl, when uric acid separates in fine crystals.

Properties.—Uric acid separates from its solution as a white crystalline powder, which is insoluble in alcohol, difficultly soluble in water, and moderately so in glycerin. On heating alone it decomposes with formation of urea, cyanic, and cyanuric acids, and CO_2; while on heating with HI, glycocoll, NH_3, and CO_2 are produced. It acts as a weak dibasic acid, and forms difficultly soluble salts, its acid properties being due to the imido (NH) groups which it contains.

Identification.—Uric acid may be detected by the reddish-purple colour of *murexide* (acid ammonium purpurate) which is produced when it is evaporated to dryness with HNO_3, and the pink residue so obtained is treated with ammonia. If potash is employed instead of ammonia, a violet-blue colour is obtained.

SECTION IV.

DERIVATIVES OF UNSATURATED HYDROCARBONS.

CHAPTER XXVII.

DERIVATIVES OF THE OLEFINES.

JUST as the paraffins yield haloid substitution products, alcohols, esters, acids, etc., so do the olefines, although their number is not so great, and, with certain exceptions, they need not be discussed in an elementary work; the **allyl** compounds being the most noteworthy.

MONO-HALOGEN DERIVATIVES OF THE OLEFINES.

Chlor-ethylene, $CH_2{:}CHCl$, *vinyl chloride*, cannot be prepared by the action of chlorine upon ethylene, because the chlorine forms ethylene chloride. If, however, ethylene chloride or ethylidene chloride is *gently* treated with alcoholic potash, one molecule of HCl is abstracted, and this gas is formed—

$$CH_2Cl.CH_2Cl + KOH = CH_2{:}CHCl + KCl + H_2O$$

The reaction is quite analogous to that for the formation of ethylene from C_2H_5I (p. 54).

Properties.—It is a colourless gas, which smells like garlic, condenses to a liquid, b.p. $-16°$, and readily undergoes polymerisation in sunlight.

Brom-ethylene, $CH_2{:}CHBr$, *vinyl bromide*, and **iodo-ethylene,** $CH_2{:}CHI$, *vinyl iodide*, are formed analogously to the chlorine derivative. The former is a liquid, b.p. 16°, sp. gr. 1·516 at $\frac{14°}{4°}$, the latter an oil smelling like garlic, b.p. 56°, sp. gr. 2·08 at $\frac{0°}{}$.

Allyl Iodide, $CH_2I.CH:CH_2$, can be prepared by the action of phosphorus and iodine upon allyl alcohol, but it is usual to act upon glycerin with those reagents (see p. 70)—

$$C_3H_5(OH)_3 + 3HI = C_3H_5I + 3H_2O + I_2$$

†*Process.*—Introduce 150 grams of dry glycerin into a half-litre tubulated retort along with 105 grams of iodine. Connect the tubulus of the retort by wide indiarubber tubing to a flask containing 35 grams of white phosphorus, cut into pieces about the size of a pea and well dried, and pass a current of CO_2 through the whole apparatus. Drop the phosphorus into the retort *little by little* by tilting the small flask, starting the reaction if required by warming gently. The distillation must proceed so that the allyl iodide distils as it is formed, and is continued till the glycerin begins to carbonise. Wash the lower layer of the distillate with soda, dehydrate over $CaCl_2$, and rectify, collecting the portion distilling between 98° and 102°, which is nearly pure allyl iodide, apart. This still contains propylene iodide and allyl alcohol, and can be purified by forming the mercury compound, recrystallising it, and then decomposing it with iodine (see below).

Properties.—Allyl iodide is a colourless liquid, b.p. 102·7°, sp. gr. 1·8696, which smells like garlic. Nascent hydrogen reduces it to propylene (Zn and HCl, or the wet Zn-Cu couple). It combines with mercury to form allyl mercuric iodide, C_3H_5HgI, which iodine decomposes, liberating the iodide—

$$C_3H_5HgI + I_2 = C_3H_5I + HgI_2$$

The **di-haloid olefines** result from combination of the halogens with acetylene. Generally speaking, the haloid olefines resemble the olefines themselves in readily combining with the halogens, halogen hydrides, and hypochlorous acid, and many undergo polymerisation with ease.

MONO-HYDRIC ALCOHOLS OF THE ALLYL SERIES, $C_nH_{2n-1}OH$.

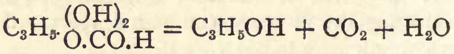
The best-known alcohol of the series is allyl alcohol, C_3H_5OH. The simplest member of it would be vinyl alcohol, which is yet unknown, since all reactions which might be expected to yield it, by a molecular transformation, give acetaldehyde instead, *i.e.* $CH_2:CH.OH$ becomes $CH_3.CHO$.

This molecular change is general; the group $=C:CH.OH$ always actually becomes $=CH.CHO$.

Allyl Alcohol, $C_3H_5OH = CH_2:CH.CH_2OH$, is found in very small quantity in crude wood spirit. (1) The earliest method of formation was the decomposition of allyl oxalate (obtained by the action of silver oxalate upon allyl iodide) by dry gaseous ammonia. This produces oxamide and allyl alcohol, which latter can be distilled off—

$$C_2O_2(C_3H_5O)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2C_3H_5OH$$

(2) A better method is by heating allyl iodide with 20 parts of water in a closed tube at 100° C.; but (3) the method usually employed for preparing it is the distillation of oxalic acid and glycerin. This depends upon the formation of mono-formin, which breaks up on heating into allyl alcohol, carbon dioxide, and water, thus—



$$C_3H_5.\genfrac{}{}{0pt}{}{(OH)_2}{O.CO.H} = C_3H_5OH + CO_2 + H_2O$$

Compare this reaction with that used in preparing formic acid (p. 137).

†*Process.*—Heat 200 grams of glycerin, 50 grams of crystallised oxalic acid, and 0·5 gram of NH_4Cl in a retort to 190° C. Change the receiver at that temperature, collect the distillate to 260°, rectify the distillate, which contains acrolein, allyl formate, and glycerin, besides allyl alcohol, by distillation. Next dry, first over K_2CO_3, then over KOH, and distil. The alcohol so procured boils at 90°, and can be completely dehydrated by means of CaO or BaO.

Properties.—Allyl alcohol is a colourless mobile liquid, b.p. 96·6°, sp. gr. 0·8706 at $\frac{0^\circ}{0^\circ}$, and solidifies at -50°. It has a pungent odour and burning taste is miscible with water, alcohol, and ether. It burns with a bright flame. Oxidation with chromic acid yields *formic acid* and carbon dioxide, while, if oxidised by silver oxide, it yields acrolein and acrylic acid. Nascent hydrogen (Zn and H_2SO_4) forms n-propyl alcohol.

Solid KOH at 150° also produces n-propyl alcohol, along with formic acid and other oxidation products. Being unsaturated, allyl alcohol combines with two atoms of a halogen to form a halogen hydrin of glycerin, and with one molecule of cyanogen to form a cyanhydrin. The last two reactions show it to contain two atoms of hydrogen less than propyl alcohol; and, as it also yields on oxidation an aldehyde, and an acid, which contain the same number of carbon atoms that it does, the only possible *constitutional* formula is that assigned to it.

ESTERS OF ALLYL ALCOHOL.

Amongst the esters of this alcohol two only will be mentioned, viz. the sulphide and the iso-thiocyanate.

Allyl Sulphide, $(C_3H_5)_2S$, is the principal constituent of oil of garlic, obtained by distilling that plant with water, and is also found in other plants. It may be artificially prepared by acting upon allyl iodide with an alcoholic solution of potassium sulphide—

$$2C_3H_5I + K_2S = (C_3H_5)_2S + 2KI$$

Properties.—Allyl sulphide is a strongly refractive liquid with an odour of garlic, b.p. 140°. It forms crystalline precipitates with $PtCl_4$, $AuCl_3$, $AgNO_3$, and other salts.

Allyl mustard oil, or **Allyl iso-thiocyanate,** $C_3H_5N{:}CS$, *allyl thiocarbimide,* is found in the oil distilled from black mustard-seed, and is also present in garlic and horseradish.

Black mustard-seed contains a glucoside called potassium myronate, which is decomposed in the presence of water by an unorganised ferment called *myrosin,* which is also contained in the seeds, according to the equation—

$$C_{10}H_{18}NS_2O_{10}K = C_3H_5N{:}CS + C_6H_{12}O_6 + KHSO_4$$

The mustard oil is also formed by a molecular transposition when allyl iodide is acted upon by an alcoholic solution of potassium thiocyanate.

Properties.—Allyl mustard oil is an oil, b.p. 151°, sp. gr. 1·028, with a pungent odour and a burning taste, and blisters the skin.

UNSATURATED ALDEHYDES, $C_nH_{2n-2}O$.

These aldehydes are related to the alcohols of the allyl series in the same way that acetaldehyde is to ethyl alcohol. The lowest member of this series—

Acrylic Aldehyde or Acrolein, $CH_2:CH.CHO$, is the very pungent liquid obtained when fats are heated, its formation being due to the glycerol which they contain. It can be formed (1) by oxidation of allyl alcohol, since that contains a primary alcoholic group; and (2) by dehydrating glycerin with potassium bisulphate or phosphorus pentoxide—

$$C_3H_5(OH)_3 - 2H_2O = C_3H_4O$$

†*Process.*—Distil together 50 grams glycerin (anhydrous) and 100 grams $KHSO_4$, and redistil the product over lead oxide.

Properties.—Acroleïn is a colourless, mobile, refractive liquid with a burning taste, b.p. 52·4°, sp. gr. 0·841 at $\frac{20^\circ}{4^\circ}$. Its vapour is very pungent, and intensely irritating to the nose and eyes. It is slightly soluble in water.

Like other aldehydes, it is a strong reducing agent; thus it reduces ammoniacal $AgNO_3$ solution, with formation of a mirror, and production of acrylic acid. Acroleïn is reduced by Zn and HCl to allyl alcohol. It reacts with NH_3 to form a red amorphous substance, *water being eliminated;* and combines with *two* molecules of $NaHSO_3$ (*difference from fatty aldehydes*). PCl_5 forms allylene chloride, and Br_2 forms di-brom-propionic aldehyde. When impure, acroleïn readily passes into *disacryl,* a white amorphous mass which is isomeric or polymeric.

Crotonic Aldehyde, $CH_3.CH:CH.CHO$, *croton aldehyde,* is of interest as being a condensation product of acetaldehyde when it is heated with zinc chloride and water to 100°. Hydrochloric acid or sodium acetate will also effect the change. Its formation by the first method depends upon the preliminary production of **aldol,** which then loses water, forming the aldehyde—

$$\begin{aligned} 2CH_3.CHO &= CH_3.CH(OH).CH_2.CHO \\ &= CH_3.CH:CH.CHO + H_2O \end{aligned}$$

Properties.—Crotonic aldehyde is a pungent mobile liquid, b.p. 105°, sp. gr. at $\frac{0^\circ}{}$ 1·033. It is soluble in water, and is oxidised by air or silver oxide to crotonic acid.

UNSATURATED MONO-BASIC ACIDS. ACIDS OF THE ACRYLIC OR OLEIC SERIES.

Acrylic acid,	C_2H_3COOH
Crotonic acid,	C_3H_5COOH
Oleic acid,	$C_{17}C_{33}COOH$, etc.

These acids are related to the allylic series of alcohols, just in the same way that acetic acid is related to ethyl alcohol.

$CH_3.CH_2OH$ Ethyl alcohol	$CH_3.CHO$ Acetaldehyde	$CH_3.COOH$ Acetic acid
$C_2H_3.CH_2OH$ Allyl alcohol	$C_2H_3.CHO$ Acroleïn	$C_2H_3.COOH$ Acrylic acid

Acrylic Acid, $CH_2{:}CH.COOH$, may be readily produced (*1) by the oxidation of acroleïn—

$$CH_2{:}CH.CHO + O = CH_2{:}CH.COOH$$

Process.—Pour a mixture of 1 part acroleïn and 3 parts of water upon freshly precipitated Ag_2O suspended in water and contained in a vessel screened from the light. When the reaction is over, heat gently to the boiling point, and add Na_2CO_3 till the whole is slightly alkaline. Evaporate the filtrate to dryness, and distil the residue with dilute H_2SO_4. Form the silver or lead salt, dry it, and decompose in a current of H_2S at 170°.

Acrylic acid is also produced (*2) by the action of alcoholic KOH upon β-iodo-propionic acid[1]—

$$CH_2I.CH_2.COOH + 2KOH = CH_2{:}CH.COOK + KI + 2H_2O$$

(compare the action of KOH on C_2H_5I, p. 54). (*3) It can be formed by distillation of β-hydroxy-propionic (hydracrylic) acid—

$$CH_2OH.CH_2.COOH = CH_2{:}CH.COOH + H_2O$$

(compare formation 1 of olefines, p. 56).

Properties.—Acrylic acid is a colourless liquid with a pungent

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[1] Halogen, hydroxyl, or other derivatives of alcohols, aldehydes, or acids, are named according to the position of the substituent to the CH_2OH, CHO, or COOH groups, *e.g.* if a halogen atom is attached to the adjacent carbon atom of an acid, it will form an α halogen acid; if to the second, a β compound; to the third, a γ derivative, and so forth. Thus $CH_3.CHI.COOH$ and $CH_2I.CH_2.COOH$ are α and β iodo-propionic acids respectively.

acid odour (not unlike that of acetic acid), b.p. 140°. It is miscible with water. It is converted into propionic acid by nascent hydrogen (boiling with Zn and H_2SO_4) or by the action of sodium amalgam—

$$CH_2{:}CH.COOH + H_2 = CH_3.CH_2.COOH$$

It unites with one molecule of bromine to give α-β-brompropionic acid, and with HI and HOCl yields β-derivatives of propionic acid—

$$CH_2{:}CH.COOH + Br_2 = CH_2Br.CHBr.COOH$$

$$CH_2{:}CH.COOH + HI = \underset{\beta\text{-iodopropionic acid}}{CH_2I.CH_2.COOH}$$

$$CH_2{:}CH.COOH + HOCl = \underset{\beta\text{-chlorlactic acid}}{CH_2Cl.CH(OH).COOH}$$

On heating with an aqueous solution of NaOH to 100°, it is changed into hydracrylic acid (see formation 3 above). On fusion with KOH it is characteristically oxidised, rupture of the molecule taking place at the double linkage, salts of formic and acetic acids being produced—

$$CH_2{:}CH.COOK + KOH + H_2O = H.COOK + CH_3.COOK + H_2$$

With the exception of the silver salt, its salts are readily soluble in water, and give off part of their acid at 100°, leaving basic compounds.

Ordinary Crotonic Acid, $CH_3.CH{:}CH.COOH$, is obtained by oxidising croton aldehyde, or from allyl iodide by the successive action of KCN and alcoholic KOH—

$$C_3H_5I + KCN = C_3H_5CN + KI$$

$$C_3H_5CN + KOH + H_2O = C_3H_5COOK + NH_3$$

It crystallises in needles, m.p. 72°, b.p. 182°. It is reduced by Zn and H_2SO_4 to n-butyric acid, and breaks up on fusion with KOH into two molecules of acetic acid.

Amongst the higher homologues of this series, special note should be taken of—

Oleic Acid, $C_{18}H_{34}O_2$.—This acid is found as tri-olein in many natural fats and oils, especially in olive oil, almond oil, and cod-liver oil. Large quantities of it are obtained as a by-product of stearin-candle manufacture. It may be prepared most readily by saponifying either olive or almond oil by caustic potash—

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3KOH = 3C_{18}H_{33}KO_2 + C_3H_5(OH)_3$$

†*Process.*—Saponify olive oil by boiling with excess of KOH. Acidify the mixture, and heat the separated acids with lead oxide for some hours at 100°. Dissolve out the lead oleate from the lead soaps formed, by ether. Acidify the ethereal solution with HCl, and filter from the precipitated $PbCl_2$. Evaporate the filtrate till free from ether, neutralise with ammonia, and add $BaCl_2$ solution to precipitate barium oleate. Recrystallise the barium salt from alcohol, and separate the oleic acid by the addition of tartaric acid.

The impure oleic acid from candle manufacture (see p. 156) may also be used in the preparation of the pure substance, and, if freshly made, contains very few oxidation products.

Properties.—Pure oleic acid forms, below 14°, a white crystalline mass, but over 14° it is a colourless, odourless oil, which *does not redden litmus.* If, however, it is exposed to the air, it absorbs oxygen, becomes yellow, acquires a rancid smell and an acid reaction. It boils at 286° at 100 mm. pressure, and distils in a current of steam at 250°. Bromine forms dibrom-stearic acid, and HI and P reduce it to stearic acid. Nitrous acid transforms it into the isomeric solid **elaïdic acid.**

Ricinoleic Acid, $C_{17}H_{32}(OH).COOH$, *hydroxyoleic acid,* occurs in castor oil as a glyceride. It crystallises to a white mass, forms a solid di-bromide, and nitrous acid forms **ricinelaïdic acid.**

GENERAL REMARKS.

Many of these acids occur in fats and oils, and the synthetical reactions illustrated in considering acrylic acid are of general application.

Properties.—These acids resemble those of the acetic series in their physical properties, *e.g.* solubility, acidity, etc.; chemically, however, they differ considerably, because they contain the group $=C:C=$, and therefore two atoms of hydrogen less than that series. They are consequently capable of combining with halogens, halogen acids, and hydrogen in the manner already exemplified. Their decomposition on fusion with KOH is also quite characteristic, acetic acid being usually one of the acids produced.

CHAPTER XXVIII.

ACETYLENE DERIVATIVES.

ALCOHOLS, $C_nH_{2n-3}OH$.

THE halogen derivatives of the acetylenes are comparatively unimportant, and only a few alcohols of the series are known. Of these, propargyl alcohol is the only one which must be considered a true acetylene derivative.

Propargyl Alcohol, $CH⋮C.CH_2OH$, *propinyl alcohol*, is produced when β-brom-allyl alcohol is heated with caustic potash and water; the liquid is then saturated with carbon dioxide, water added, and the alcohol distilled off. It can be separated from the distillate by carbonate of potash, and dried over lime—

$$CHBr{:}CH.CH_2(OH) + KOH = CH⋮C.CH_2(OH) + KBr + H_2O$$

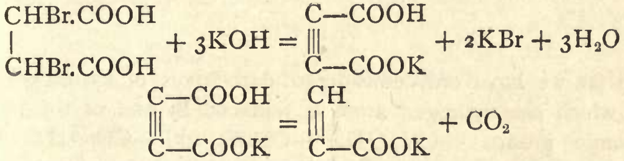
Properties.—Propargyl alcohol is a colourless, pleasant-smelling, mobile liquid, b.p. 114°–115°, and sp. gr. 0·9628 at 21°. Since it contains the group $HC⋮C—$, as well as a hydroxyl group, it has two hydrogen atoms replaceable by metals, and ammoniacal copper and silver solutions respectively yield the explosive compounds $Cu_2(C_3H_2OH)_2$ and $C_3H_2(OH)Ag$. It unites directly with bromine and HBr to form di- and mono-brom-allyl alcohols; PCl_3 and PBr_3 respectively displace the OH group by Cl or Br. It is decomposed by fusion with KOH, with formation of acetylene, potassium formate, and hydrogen.

UNSATURATED ACIDS FROM ACETYLENE.

PROPIOLIC ACID, $C_2H.COOH$
LINOLEIC ACID, $C_{17}H_{31}COOH$

Of these acids, which contain *four* atoms of hydrogen less than the corresponding ones of the acetic series, the best known is—

Propiolic Acid, $CH\vdots C.COOH$, the potassium salt of which is obtained by gently heating an aqueous solution of the mono-potassium salt of acetylene di-carboxylic acid (obtained by the action of alcoholic potash on dibrom- or iso-dibrom-succinic acid)—



$$\begin{array}{l}\mathrm{CHBr.COOH}\\ |\\ \mathrm{CHBr.COOH}\end{array} + 3\mathrm{KOH} = \begin{array}{l}\mathrm{C{-}COOH}\\ |||\\ \mathrm{C{-}COOK}\end{array} + 2\mathrm{KBr} + 3\mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{C{-}COOH}\\ |||\\ \mathrm{C{-}COOK}\end{array} = \begin{array}{l}\mathrm{CH}\\ |||\\ \mathrm{C{-}COOK}\end{array} + \mathrm{CO_2}$$

Properties.—Propiolic acid, liberated from the above salt, crystallises in silky needles, which melt at 6° C., and it boils with decomposition at 144°. It has a smell very like acetic acid.

Being unsaturated, it can unite directly with the halogens, etc., forming first olefine, and then paraffin derivatives. It is reduced by sodium amalgam to propionic acid. Its potassium salt yields explosive compounds with ammoniacal silver and cuprous solutions.

Linoleic Acid, $C_{17}H_{31}O_2$, is found as an ester of glycerin in *drying* oils, such as linseed oil, hemp oil, and poppy oil, as well as in smaller quantities in many others. It is obtained by saponification of linseed oil, and purified by means of its barium salt, which is soluble in ether. It is a yellow oil, sp. gr. 0·92, insoluble in water. It is reduced by HI and P to stearic acid, and bromine forms tetra-brom stearic acid (compare Oleic acid).

SECTION V.

DIHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

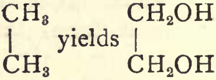
CHAPTER XXIX.

GLYCOLS.

So far we have only considered derivatives of hydrocarbons in which *one* hydrogen atom is replaced by one of the monatomic groups $—CH_2.OH$, $—CO.H$, or $—CO.OH$. We have now to study those in which *two* hydrogen atoms are replaced, so yielding dihydric alcohols, di-aldehydes, di-basic acids, or intermediate substances possessed of the characters of any two of those classes.

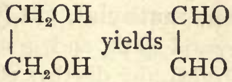
These bodies will be found possessed of many of the characteristics of similar monovalent compounds, as well as of special properties due to the fact that they are divalent derivatives. Many of the methods of preparation will be entirely analogous to those already given for the production of the analogous monovalent compounds.

The simplest of these substances known in a free state is the dihydric alcohol **glycol**. This may be considered as derived from ethane by the replacement by hydroxyl of one of the hydrogen atoms attached to each of the two carbon atoms—



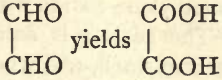
$$\begin{array}{lcl} CH_3 & & CH_2OH \\ | & \text{yields} & | \\ CH_3 & & CH_2OH \end{array}$$

It will be noticed that glycol contains the group $—CH_2OH$ twice, and is therefore a di-*primary* alcohol. By the careful oxidation of this body the di-aldehyde glyoxal can be procured—

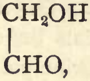
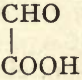
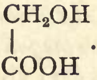


$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}\ \text{yields}\ \begin{array}{c}CHO\\|\\CHO\end{array}$$

And this, in its turn, can be oxidised to oxalic acid—



$$\begin{array}{c}CHO\\|\\CHO\end{array}\ \text{yields}\ \begin{array}{c}COOH\\|\\COOH\end{array}$$

There are, however, a number of intermediate compounds producible by suitable methods; thus, besides the above-named, there may be produced glycollic aldehyde,  $\begin{array}{c}CH_2OH\\|\\CHO\end{array}$, glyoxylic acid,  $\begin{array}{c}CHO\\|\\COOH\end{array}$, and glycollic acid,  $\begin{array}{c}CH_2OH\\|\\COOH\end{array}$. Other dihydric alcohols form similar series.

The hydroxyl groups of the alcohols may be partly or entirely replaced, according to circumstances, by other radicles, such as acetyl, amidogen, cyanogen, chlorine, and bromine, in exactly the same way as those of the monohydric alcohols.

The dihydric alcohols, similarly to the monohydric, may be classed as primary, secondary, and tertiary, according to the manner in which the hydroxyl groups are substituted in the parent hydrocarbon; but it must be remembered that glycols in which the hydroxyl groups are both attached to the *same* carbon atom are not known in the free state, but that reactions which we should expect to yield them actually produce aldehydes.

DIHYDRIC ALCOHOLS, OR GLYCOLS.

The first member of this series is—

Methylene Glycol, $CH_2(OH)_2$, *formic ortho-aldehyde*, which is not known to exist free, although it is supposed by some that it is present in the solution produced by heating para-formaldehyde (p. 123) with water to 130°; the reactions, however, by which we should expect to obtain it always yield its anhydride, *i.e.* formaldehyde. But though its existence free is not certain, we are acquainted with several of its derivatives, *e.g.* the di-methyl ether, **methylal,** $CH_2(OCH_3)_2$, is obtained by the oxidation of wood spirit, and is an aromatic-smelling liquid, b.p. 42°. **Ethylal,** the di-ethyl ether, is also known, and **methylene acetate,** $CH_2(C_2H_3O_2)_2$, an oily liquid obtained by heating methylene iodide with silver acetate, may also be mentioned. The acetate is soluble in water, has a strongly pungent taste and smell, and when heated in a sealed tube for some hours to 100° does not yield the glycol, but para-formaldehyde.

Glycol, $CH_2OH.CH_2OH$, *ethene glycol, ethylene alcohol,* can be obtained by methods which are quite the same in principle as those employed to prepare monohydric alcohols (p. 94). (*The student should carefully refer to these, and compare them with the following methods.*)

Thus (*1) glycol can be prepared from ethylene iodide by treating it with silver acetate and saponifying the resultant product with potash—

$$\text{(i.)}\quad C_2H_4I_2 + 2Ag\bar{A} = C_2H_4\bar{A}_2 + 2AgI$$
$$\text{(ii.)}\quad C_2H_4\bar{A}_2 + 2KOH = C_2H_4(OH)_2 + 2K\bar{A}$$

It can also be prepared from ethylene bromide by the successive action of potassium acetate and potash, or by heating it with PbO and water to 150°, or by heating with water only to 100° in sealed tubes—

$$C_2H_4Br_2 + 2H_2O = C_2H_4(OH)_2 + 2HBr$$

†*Process.*—A modification of the last process is usually employed. Boil 188 grams of ethylene bromide with 138 grams of K_2CO_3 and 1 litre of water in a flask provided with an inverted condenser. When the whole of the bromide is dissolved, concentrate the liquid on the water-bath, filter from the crystals of KBr which are formed, and wash them with alcohol. Distil the alcoholic filtrate, and collect apart the portion that distils between 185° and 205°. Redistil that fraction, and collect that which comes over between 195° and 200° as glycol. The yield is small.

A considerable proportion of vinyl bromide, C_2H_3Br

escapes during the process as the result of a secondary reaction, and may be condensed in bromine.

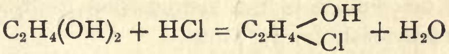
The fundamental reaction is represented thus—

$$C_2H_4Br_2 + H_2O + K_2CO_3 = C_2H_4(OH)_2 + 2KBr + CO_2$$

the reaction which results in the formation of the vinyl bromide being—

$$C_2H_4Br_2 + K_2CO_3 = C_2H_3Br + KBr + KHCO_3$$

Properties.—Glycol is an inodorous, colourless, syrupy liquid with a sweet taste, b.p. 198°, and sp. gr. 1·1168 at $\frac{15°}{15°}$. It is miscible with water and with alcohol, and but slightly soluble in ether. Nitric acid ultimately oxidises it to oxalic acid, but there is intermediate formation of glycollic acid, glyoxal, etc. Strong hydrochloric and hydrobromic acids react with glycol, displacing successively one or two hydroxyl groups by Cl or Br, and forming **halogen hydrins** and di-haloid derivatives respectively—



$$C_2H_4(OH)_2 + HCl = C_2H_4{<}\begin{matrix}OH\\Cl\end{matrix} + H_2O$$

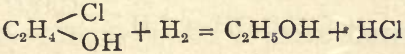
Ethylene chlorhydrin

$$C_2H_4(OH)_2 + 2HCl = C_2H_4Cl_2 + 2H_2O$$

Ethylene chloride

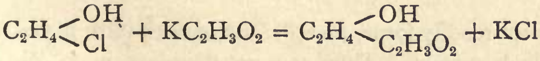
The second OH group is, however, much more readily displaced by the employment of phosphorus haloid compounds than by the haloid acids themselves.

The halogen hydrins can readily be reduced to alcohols by the action of nascent hydrogen—



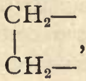
$$C_2H_4{<}\begin{matrix}Cl\\OH\end{matrix} + H_2 = C_2H_5OH + HCl$$

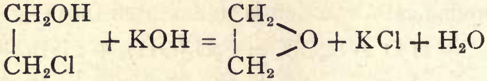
They react with the salts of acids to form basic esters of the particular acid; *e.g.*—



$$C_2H_4{<}\begin{matrix}OH\\Cl\end{matrix} + KC_2H_3O_2 = C_2H_4{<}\begin{matrix}OH\\C_2H_3O_2\end{matrix} + KCl$$

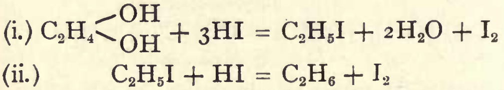
Mono-acetin

and if treated with potassium hydrate they yield the **oxide** of the di-valent radicle  $\begin{matrix}CH_2—\\|\\CH_2—\end{matrix}$, **ethylene oxide,** which is a liquid isomeric with acetaldehyde, and slowly absorbs water, re-forming glycol—


Ethylene oxide

It is readily soluble in water, neutral in reaction, strongly basic in character, precipitates metallic hydroxides from solutions of their salts, unites with acetic acid to form the mono-acetate, with acetic anhydride to form the di-acetate of glycol, with hydrochloric acid to form chlorhydrins, with ammonia to form the hydramine $C_2H_4<\genfrac{}{}{0pt}{}{OH}{NH_2}$ and with $NaHSO_3$ it yields $CH_2OH.CH_2SO_3Na$.

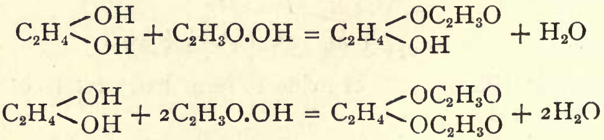
Hydriodic acid acts upon glycol differently to hydrochloric or hydrobromic acid. If suitable proportions are used, ethyl iodide is formed; but if excess of the acid is employed, reduction takes place to the hydrocarbon itself, as has been explained previously (p. 47); thus—



$$\text{(i.)}\ C_2H_4<\genfrac{}{}{0pt}{}{OH}{OH} + 3HI = C_2H_5I + 2H_2O + I_2$$

$$\text{(ii.)}\ C_2H_5I + HI = C_2H_6 + I_2$$

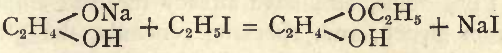
The oxygen acids act upon glycol, forming basic or neutral esters. So, for example, from glycol and acetic acid, aided by heat, **glycollic mono- and di-acetin** may be produced; thus—



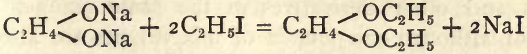
$$C_2H_4<\genfrac{}{}{0pt}{}{OH}{OH} + C_2H_3O.OH = C_2H_4<\genfrac{}{}{0pt}{}{OC_2H_3O}{OH} + H_2O$$

$$C_2H_4<\genfrac{}{}{0pt}{}{OH}{OH} + 2C_2H_3O.OH = C_2H_4<\genfrac{}{}{0pt}{}{OC_2H_3O}{OC_2H_3O} + 2H_2O$$

Glycol readily forms metallic derivatives (**the glycollates**) with alkali metals. Thus sodium dissolves in it, displacing hydroxylic hydrogen and forming the mono-sodium derivative; and if that is heated with the metal, the second hydroxyl hydrogen atom is displaced. These compounds are decomposed by water with the re-formation of glycol; and they react with alkyl iodides to produce ethers in the same manner that ordinary ethers are formed from alcoholates (see p. 105)—



$$C_2H_4{<}\substack{ONa\\OH} + C_2H_5I = C_2H_4{<}\substack{OC_2H_5\\OH} + NaI$$



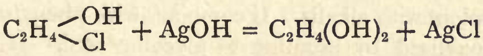
$$C_2H_4{<}\substack{ONa\\ONa} + 2C_2H_5I = C_2H_4{<}\substack{OC_2H_5\\OC_2H_5} + 2NaI$$

Constitution.—Glycol behaves throughout in its reactions as a dihydric alcohol, and the constitutional formula assigned to it is amply supported by its formation from ethylene bromide.

Ethylidene Glycol, $CH_3.CH(OH)_2$, isomeric with the ethylene compound, is not known free, but its alkyl ethers, the **acetals,** are well known. The principal of these, **acetal,** $CH_3.CH(OC_2H_5)_2$, *ethylidene di-ethyl ether*, is formed (1) by the oxidation of alcohol (see Chloral, p. 130); and (2) by the action of sodium ethylate upon ethylidene bromide. It is a colourless liquid with an agreeable odour, b.p. 104°. Dilute acids break it up readily into alcohol and aldehyde.

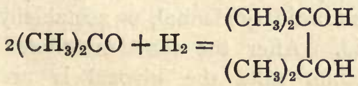
General Remarks on the Glycols.

The glycols or dihydroxy-paraffins are prepared from dihaloid paraffins by methods already illustrated in discussing glycol itself, but besides these processes they may be prepared from the chlorhydrins which are readily produced from the olefines by addition of HOCl. If the chlor-hydrins are treated with moist silver oxide, the glycol is formed—



$$C_2H_4{<}\substack{OH\\Cl} + AgOH = C_2H_4(OH)_2 + AgCl$$

And, lastly, the di-tertiary glycols, or **pinacones,** are produced by the action of nascent hydrogen (sodium amalgam) on ketones; *e.g.*—



$$2(CH_3)_2CO + H_2 = \begin{array}{c}(CH_3)_2COH\\ | \\ (CH_3)_2COH\end{array}$$

Properties.—The glycols are colourless, viscous liquids with neutral reaction; the lower members of the series have a sweet, the higher a rather bitter, taste. They are readily soluble in water, slightly soluble in ether, and they boil at higher temperatures than the corresponding monohydric alcohols. Their reactions with halogens, halogen hydrides, PCl_5, PBr_3, acids, etc., have already received ample illustration from glycol; and, speaking generally, the glycols form esters and other derivatives in the same manner as ethyl alcohol, although compounds of mixed types are also formed owing to the divalency of the radicles, ethylene, propylene, etc.

CHAPTER XXX.

OXIDATION PRODUCTS OF GLYCOLS.

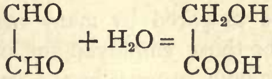
IT has been already stated (p. 217) that glycol forms by oxidation the aldehydic substances glycollic aldehyde, glyoxal, and glyoxylic acid.

Glycollic Aldehyde, $CH_2OH.CHO$, is the first oxidation product of glycol, and is the simplest example of the alcoholic aldehydes, of which glucose is so well known a type. It can be prepared from glycol-acetal, $CH_2OH.CH(OC_2H_5)_2$, by hydrolysis with *very* dilute mineral acids; *e.g.* boil the acetal with an equal quantity of water and a few drops of H_2SO_4 till no further oily drops separate on dilution. Then precipitate the acid by $BaCO_3$, and distil off the alcohol.

Properties.—It is a liquid which is volatile in steam, reduces alkaline copper solutions at ordinary temperatures, and gives a yellow colour with alkalis. It combines with phenyl-hydrazine, and is oxidised by bromine to glycollic acid. It is readily polymerised.

Glyoxal, CHO.CHO, the di-aldehyde derived from glycol, is readily produced along with glyoxylic and glycollic acids, etc., when ordinary alcohol, or acetaldehyde, is oxidised with nitric acid. After the above-mentioned acids are got rid of as calcium salts, the glyoxal is precipitated from the solution by means of $NaHSO_3$. The crystalline compound obtained is transformed into the barium salt, and on decomposition of that with dilute H_2SO_4 a solution is obtained which yields the aldehyde on evaporation.

Properties.—Glyoxal is an amorphous, deliquescent solid, soluble in alcohol and ether. It acts as an aldehyde, combining with $NaHSO_3$ and reducing ammoniacal silver solutions. Water at 150°, or alkalis in the cold, form glycollic acid, one aldehydic group being oxidised, and the other reduced—



$$\begin{matrix}CHO\\ |\\ CHO\end{matrix} + H_2O = \begin{matrix}CH_2OH\\ |\\ COOH\end{matrix}$$

A small quantity of HNO_3 forms glyoxylic acid; a larger amount, oxalic acid.

Another oxidation product of glycol is the aldehyde acid—

Glyoxylic Acid, $CHO.COOH$, or *glyoxalic acid.*—This acid behaves in many ways as if it possesses the formula $COOH.CH(OH)_2$ (analogous to chloral hydrate), *i.e.* it appears to be a derivative of ethylidene glycol. It has, however, true aldehydic properties, and will be considered here. It can be produced (1) by the slow oxidation of alcohol, acetaldehyde, or glycol by nitric acid; *e.g.*—

$$CH_3.CH_2OH + 2O_2 = CH(OH)_2.COOH + H_2O$$

(2) It is better prepared by heating di-bromacetic acid with water in a closed vessel for 24 hours to 150°—

$$CHBr_2.COOH + 2H_2O = CH(OH)_2.COOH + 2HBr$$

Properties.—Glyoxylic acid forms a thick syrup, sp. gr. 1·3, which crystallises on standing over strong H_2SO_4 in crystals, which have the formula $COOH.CH(OH)_2$. It has a taste like tartaric acid, and decomposes when strongly heated, but distils unchanged in a current of steam.

As an *aldehyde*, it reduces ammoniacal silver solutions, and unites with $NaHSO_3$, and with phenyl-hydrazine.

As an *acid*, it forms salts with metals; of these, the NH_4 and K salts appear to be salts of the aldehyde acid, the others are derivatives of the alcoholic acid. Glyoxylic acid is oxidised to oxalic acid by HNO_3, and reduced to glycollic acid by zinc.

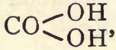
Continuing our study of the oxidation products of the glycols, we next consider an important series of acids which contain both alcoholic and acid groups, and therefore combine in themselves the properties of both those classes of bodies.

HYDROXY-CARBOXYLIC ACIDS OR MONOHYDROXY-FATTY ACIDS.

These acids are prepared by many reactions, which are simply extensions of those employed for the introduction of hydoxylic or carboxylic groups in the compounds hitherto discussed.

The earliest members of the series are—
Carbonic acid, $OH.COOH$.
Glycollic acid, $CH_2(OH).COOH$.
Lactic acids, $CH_2(OH).CH_2.COOH$ and $CH_3.CH(OH).COOH$.

The modes of preparation and properties of this series of acids will be quite sufficiently illustrated for elementary purposes by the study of these acids.

Carbonic Acid,  $\mathrm{CO}\begin{smallmatrix}\diagup \mathrm{OH} \\ \diagdown \mathrm{OH}\end{smallmatrix}$, *hydroxy-formic acid*, may be viewed as the first of this series of acids, but has not been isolated. Well-known *derivatives* of this acid, however, do exist, but they differ from those of the higher members of the series, because the hydroxyl groups which may be displaced in the acid are of equal value, and hence there is no distinction between alcoholic and acid compounds. They have, therefore, already been considered apart from the acids of this series (see p. 200).

Glycollic Acid, $CH_2(OH).COOH$, *hydroxy-acetic acid*, is found in the leaves of the Virginian creeper, in the juice of unripe grapes, and as the potassium salt in the "yolk" from sheep's wool.

(*1) It was first obtained by the action of nitrous acid on glycocoll—

$$CH_2NH_2.COOH + HNO_2 = CH_2(OH).COOH + N_2 + H_2O$$

(*2) It is produced by the incomplete oxidation of glycol, using dilute HNO_3 or platinum sponge in presence of air—

$$CH_2(OH).CH_2OH + O_2 = CH_2(OH).COOH + H_2O$$

(*3) It is also an oxidation product of many other substances, *e.g.* of alcohol, aldehyde, and glycerin with nitric acid; and of glycerin, dextrose, and levulose with silver oxide. (*4) A useful synthetical method of producing it is to decompose chloracetic acid by boiling with water, or with water and $CaCO_3$—

$$CH_2Cl.COOH + H_2O = CH_2(OH).COOH + HCl$$

†*Process.*—Boil a 5 per cent. solution of chloracetic acid for some days in a flask provided with a reflux condenser. Then concentrate the product, and the glycollic acid will crystallise out in needles. The evaporation must not be carried too far, or glycollic anhydride is formed.

Properties.—Glycollic acid is a crystalline solid, m.p. 79°, which is obtained from water in needles, or from ether or alcohol in plates. If impure it deliquesces in the air; is very soluble in water, alcohol, and ether, is slightly volatile in steam, and on distillation forms para-formaldehyde. Concentrated HNO_3 oxidises it to oxalic acid, while nascent hydrogen (Zn and H_2SO_4) reduces it to *acetic acid.* A concentrated solution of HBr at 100° slowly converts it into bromacetic acid, and PCl_5 produces chloracetyl (glycolyl) chloride, $CH_2Cl.COCl$; *i.e.* both the alcoholic and carboxylic hydroxyls are replaced by chlorine, and the compound produced acts both as a chlor-paraffin and as an acid chloride.

This may be shown by its reaction with water or alcohol, by which the chlorine attached to the carbonyl group is displaced, with the respective production of an acid or an ester—

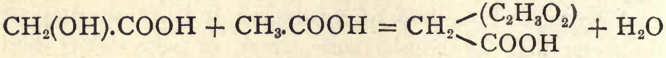
$$CH_2Cl.COCl + H_2O = CH_2Cl.COOH + HCl$$

The remaining chlorine atom is only replaceable by the ordinary means employed to displace the halogen in a paraffin.

Glycollic acid forms salts which are usually readily soluble in water, the calcium salt and silver salt being exceptions. The alkali salts are very deliquescent.

Since glycollic acid contains both the CH_2OH and COOH groups, it can form ethers or esters in which one or both of these groups interact.

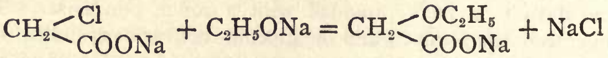
Thus the *alcoholic* OH group will react with acids, or their salts to form esters; so *e.g.*—



$$CH_2(OH).COOH + CH_3.COOH = CH_2{<}\begin{matrix}(C_2H_3O_2)\\ COOH\end{matrix} + H_2O$$

Acetoglycollic acid

and its hydroxyl can also be indirectly replaced by alkyl groups, when chloracetic acid is treated with an alcoholate, thus—



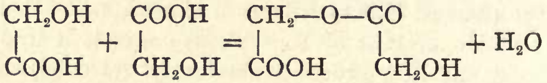
$$CH_2{<}\begin{matrix}Cl\\ COONa\end{matrix} + C_2H_5ONa = CH_2{<}\begin{matrix}OC_2H_5\\ COONa\end{matrix} + NaCl$$

Finally, the acid group may be esterified in the usual manner by passing dry HCl through a solution of the acid in the alcohol—

$$CH_2(OH).COOH + C_2H_5OH = CH_2(OH).COOC_2H_5 + H_2O$$

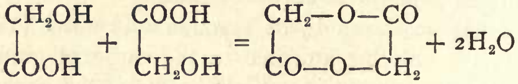
Glycollic acid forms *three* anhydrides, viz.—

1. **Glycollic Anhydride** is an *ester* formed by heating the acid to 100°, when two molecules of it mutually react—



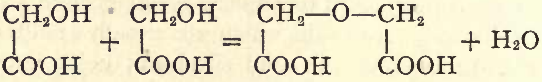
$$\begin{array}{c}CH_2OH\\ |\\ COOH\end{array} + \begin{array}{c}COOH\\ |\\ CH_2OH\end{array} = \begin{array}{lll}CH_2 & -O- & CO\\ | & & |\\ COOH & & CH_2OH\end{array} + H_2O$$

2. **Glycolide** is formed at a higher temperature, 250°, both the acid and both the alcoholic groups interacting—



$$\begin{array}{c}CH_2OH\\ |\\ COOH\end{array} + \begin{array}{c}COOH\\ |\\ CH_2OH\end{array} = \begin{array}{lll}CH_2 & -O- & CO\\ | & & |\\ CO & -O- & CH_2\end{array} + 2H_2O$$

3. **Di-glycollic Acid** is a true *ether* produced by elimination of water from the alcoholic groups only, and is formed when chloracetic acid is boiled with lime—



$$\begin{array}{c}CH_2OH\\ |\\ COOH\end{array} + \begin{array}{c}CH_2OH\\ |\\ COOH\end{array} = \begin{array}{lll}CH_2 & -O- & CH_2\\ | & & |\\ COOH & & COOH\end{array} + H_2O$$

Constitution of Glycollic Acid.—This follows readily from its production from chloracetic acid, and is supported by its formation from glycol and the behaviour of the compound formed from it by PCl_5 (see this, p. 225).

Hydroxy-propionic Acids or Lactic Acids, $C_3H_6O_3$. —Ordinary chemical formulæ only permit the prediction of two isomeric acids, viz.—

$$\underset{\alpha\text{-hydroxy-propionic acid}}{CH_3.CH(OH).COOH} \text{ and } \underset{\beta\text{-hydroxy-propionic acid}}{CH_2(OH).CH_2.COOH}$$

but it will be noticed that the formula of the former acid contains an asymmetric carbon atom, and we may therefore expect to have two α-hydroxy-propionic acids with complementary physical properties. Actually we know the inactive form produced by the mixture of the two active varieties, and we also know the dextro-rotatory compound.

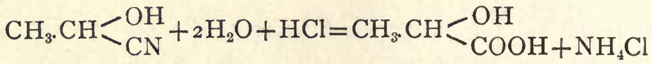
1. Lactic Acid, $CH_3.CH.(OH).COOH$, *α-hydroxy-propionic acid, fermentation lactic acid, ethylidene lactic acid.*—This acid was first discovered in sour milk, and is present in koumiss, in opium, and in the gastric juices during dyspepsia.

Lactic acid may be formed by the following methods: (1) By the lactic fermentation of sugars, starches, and gums; the ferment producing this change (*Bacterium lactis*) is shown in Fig. 44, and grows in presence of sufficient nitrogenous food.

FIG. 44.

Process.—The usual method employed is the following: Dissolve a mixture of 3 kilos. of cane sugar and 15 grams of tartaric acid in 17 kilos of boiling water. After two days add to this 1200 grams of zinc white (ZnO), along with 60 grams of putrid cheese which is suspended in 4 kilos. of sour milk. Keep this mixture at 40°–45° for 8–10 days, when a crystalline magma of zinc lactate is formed, as well as some mannitol (p. 259). Recrystallise the salt from boiling water; then dissolve in boiling water, precipitate the zinc by H_2S, and filter off the ZnS. Concentrate the filtrate by evaporation, and then extract with ether, which leaves the mannitol, and any undecomposed zinc salt, behind. The lactic acid is obtained from the ethereal solution by evaporation.

Lactic acid is also produced by the following general methods: (*2) from propylene glycol by oxidation; (*3) from α-chlor- or α-brom-propionic acids by boiling with silver oxide; (*4) from alanine, $CH_3.CHNH_2.COOH$, by HNO_2; these have been illustrated by glycollic acid. Also (*5) from ethylidene cyanhydrin (α-hydroxynitrile) by saponification with HCl; *e.g.*—



$$CH_3.CH\begin{smallmatrix}\nearrow OH\\ \searrow CN\end{smallmatrix} + 2H_2O + HCl = CH_3.CH\begin{smallmatrix}\nearrow OH\\ \searrow COOH\end{smallmatrix} + NH_4Cl$$

Hydroxy-propionitrile

The nitrile is obtained by the addition of HCN to aldehyde.

Properties.—Lactic acid, obtained as just described, is an uncrystallisable colourless syrup, sp. gr. 1·21–1·24. It has a sour taste, no smell, is hygroscopic, readily soluble in water and alcohol, not so readily in ether. It is not, however, the pure acid; it always contains some anhydride, the amount of which increases rapidly till, after the lapse of some months, it may consist entirely of that substance and **lactide** (compare Glycollic anhydride and Glycollide). When heated to 130° the syrupy acid is changed into lactide, and at higher temperatures CO, CO_2, and aldehyde are found as well. Heated with quicklime, alcohol and carbon monoxide are produced.

Dilute H_2SO_4 at 130° transforms it into aldehyde and formic acid, chromic acid mixture oxidises it to acetic acid and carbon dioxide. Hydrobromic acid forms α-brom-propionic acid, but hydriodic acid *reduces* it to propionic acid. A strong solution of potassium lactate, when subjected to electrolysis, yields aldehyde and carbon dioxide.

In its formation of anhydrides, ethers, and esters, lactic acid is quite analogous to glycollic acid (see p. 226); *e.g.* it forms the anhydrides **lactic anhydride, lactide,** and **di-lactic acid.**

Ordinary lactic acid and its salts are optically inactive, *i.e.* do not rotate the plane of polarised light. If, however, *Penicillium glaucum* is allowed to grow in a solution of ammonium lactate, the salt of the lævo-rotatory acid is destroyed, and *dextro-rotatory* **para-lactic acid,** $CH_3.CH(OH).COOH$, is obtained from the residue.

2. **Sarco-lactic Acid,** which is found in many animal juices, and in the blood after death, appears to be identical with the dextro-gyrate acid just mentioned. It can readily be obtained from Liebig's extract of beef.

Properties.—Sarco-lactic acid is obtained as a dextro-rotatory syrup, which behaves chemically like lactic acid; *e.g.* it yields lactide on heating to 140°, which gives the active acid on rehydration. Its salts are lævo-gyrate; the calcium salt is less soluble, and the zinc salt more soluble, than the corresponding lactates.

3. **Hydracrylic Acid,** $CH_2(OH).CH_2.COOH$, *β-hydroxy-propionic acid, ethylene lactic acid.*—This acid may be formed (*1) by the action of moist silver oxide on β-iodo-propionic acid—

$$CH_2I.CH_2.COOH + AgOH = CH_2(OH).CH_2.COOH + AgI$$

(2) from ethylene chlorhydrin by the action of KCN and saponification of the cyanhydrin formed;

i.e. $CH_2(OH).CH_2Cl$ yields $CH_2(OH).CH_2.CN$, and that gives $CH_2(OH).CH_2.COOH$

(*3) by oxidation of β-propylene glycol; and (4) note specially its formation from acrylic acid by addition of water, hence its name (see p. 212).

Properties.—It is a strongly acid, non-crystallisable syrup, and readily yields acrylic acid when heated alone (see p. 211) or with dilute H_2SO_4.

Chromic acid or HNO_3 oxidises it to oxalic acid and CO_2, and it is reduced by HI to β-iodo-propionic acid. It does not yield the iodoform reaction (*difference from lactic acid*), and its zinc salt is soluble in alcohol (*difference from the zinc salts of lactic and para-lactic acids*).

Constitution of the Lactic Acids.—Since the ordinary and paralactic acids are simply physical isomers, it is only necessary to distinguish chemically between lactic and hydracrylic acid. The first of these contains a secondary alcoholic group, as shown by the formation of a ketonic acid, pyruvic acid, $CH_3.CO.COOH$, when it is oxidised by potassium permanganate. This is also shown by its formation from aldehyde and HCN. These give the ethylidene cyanhydrin, which in turn yields lactic acid (see Formation 5, p. 228). This proves its constitution. On the other hand, since oxidation of hydracrylic acid yields malonic acid, $CH_2(COOH)_2$, it contains a primary alcohol group; and its constitution is fully explained by its formation from ethylene chlorhydrin (see Formation 2, p. 229), which is itself obtainable from glycol (see p. 219).

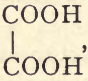
CHAPTER XXXI.

OXIDATION PRODUCTS OF GLYCOLS—Continued.

DICARBOXYLIC ACIDS.

ON further oxidation the primary glycols yield dibasic acids, which are roughly divisible into two series, according as the carboxyl groups are attached to the same or different carbon atoms. The principal acids in each group are the following:—

Oxalic acid,	$C_2H_2O_4$	Succinic acid,	$C_4H_6O_4$
Malonic acid,	$C_3H_4O_4$	Pyrotartaric acid	$C_5H_8O_4$
Iso-succinic acid,	$C_4H_6O_4$	Glutaric acid	
Ethyl malonic acid	$C_5H_8O_4$	Adipic acid,	$C_6H_{10}O_4$
Di-methyl malonic acid			

Oxalic Acid,  $\begin{array}{c}COOH\\|\\COOH\end{array}$, the first acid in the series, occurs in the free state in some fungi and the juice of the chickpea, while its salts are found in many animal and plant juices. The acid potassium salt is present in wood sorrel and in common rhubarb. Calcium oxalate is found in certain urinary calculi, in many lichens, and in different parts of many plants, often occurring as crystals, $CaC_2O_4.3H_2O$, termed "raphides."

(1) Oxalic acid is formed as the product of the oxidation of many organic materials, such as starch, sugar, and cellulose, by means of nitric acid.

†*Process.*—Gradually add 400 grams of nitric acid, sp. gr. 1·38, to 50 grams of cane sugar; heat the mixture to the boiling point, and when the reaction is over evaporate to one-sixth of its bulk. Oxalic acid crystallises out, and may be purified by recrystallisation from water.

(2) Oxalic acid is also produced by a complex reaction when starch, bran, or other vegetable substance is fused with potash, and this is the method now employed for its manufacture.

Manufacture.—Oxalic acid is made from sawdust, preferably that from soft woods, such as the pine or poplar. This is mixed with caustic lye, sp. gr. 1·35, which is made either from potash or from a mixture of 3 parts potash and 2 parts soda. Soda alone cannot be used, as it does not give a good yield. The mixture is spread out on iron plates and heated to a temperature which at first is about 200°, and is never allowed to exceed 250°. The mass swells up, becomes dry, and then evolves hydrogen and hydrocarbons, finally becoming dark brown in colour and entirely soluble. At the expiration of about 6 hours it forms a greyish mass, which contains about 20 per cent. of oxalic acid combined with alkalis. This product is treated with warm water, which dissolves out the excess of alkali and the salts of potash and soda, except the difficultly soluble sodium oxalate. The sodium oxalate is decomposed by milk of lime, and the calcium oxalate produced is in its turn decomposed by sulphuric acid. From the liquid obtained, after separation of the gypsum, the oxalic acid is obtained by crystallisation. If perfectly pure oxalic acid is wanted, the impure product may be recrystallised from a 10 per cent. solution of hydrochloric acid, and then from water, or may be carefully sublimed.

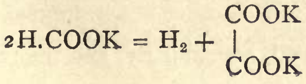
Oxalic acid is also formed by the following reactions, which are of theoretical importance. Thus—

(*3) By the oxidation of glycol or of glycollic acid—

$$CH_2(OH).CH_2OH + 2O_2 = COOH.COOH + 2H_2O$$

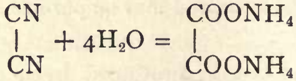
$$CH_2(OH).COOH + O_2 = COOH.COOH + H_2O$$

(4) When an alkaline formate is heated to a temperature not above 400°, an alkaline oxalate is produced—



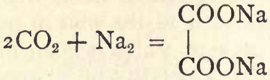
$$2H.COOK = H_2 + \begin{array}{l} COOK \\ | \\ COOK \end{array}$$

(5) When an aqueous solution of cyanogen is allowed to stand for some time, ammonium oxalate is formed—



$$\begin{array}{c} CN \\ | \\ CN \end{array} + 4H_2O = \begin{array}{c} COONH_4 \\ | \\ COONH_4 \end{array}$$

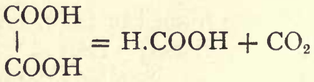
While finally, (6) the production of oxalic acid when carbon dioxide is passed over a mixture of sodium and sand, heated to 360°, is specially interesting—



$$2CO_2 + Na_2 = \begin{array}{c} COONa \\ | \\ COONa \end{array}$$

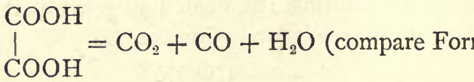
The reader should compare the last two reactions with those for the production of formic acid from HCN, and from CO_2 and potassium (see p. 138).

Properties.—Oxalic acid crystallises with two molecules of water in monoclinic prisms, sp. gr. 1·653 at $\frac{18.5^\circ}{4^\circ}$. These lose water of crystallisation when dried over concentrated H_2SO_4; but the anhydrous acid is best obtained by carefully drying the ordinary acid at 100°, and volatilising it at a temperature not exceeding 157°. Oxalic acid is readily soluble in water and fairly so in alcohol, but its aqueous solutions readily decompose. It has a strongly acid taste, and is a powerful acid, *e.g.* it decomposes both sodium chloride and nitrate on heating, as well as many other salts. When heated quickly to a high temperature it yields formic acid and CO_2—



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} = H.COOH + CO_2$$

also when heated with glycerin (see p. 137). When heated with strong H_2SO_2 it breaks up without blackening, thus—



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} = CO_2 + CO + H_2O$$ (compare Formic acid)

P_2O_5, PCl_5, and PCl_3 act similarly, and the two latter reagents do *not* produce acid chlorides. Oxalic acid is a strong reducing agent; *e.g.* it precipitates the metals from solutions of platinum, gold, or silver salts, for which reason it is employed as a developer in photography. It also readily reduces acid solutions of $KMnO_4$ and $K_2Cr_2O_7$, and hence finds employment in volumetric analysis. It can be itself reduced (by the zinc-copper couple) to glycollic acid. Oxalic acid finds employment in calico-printing, in various bleaching processes, in the manufacture of certain artificial colours, as a cleansing agent, etc.

The *constitution* of oxalic acid follows from its formation from glycol, cyanogen, and sodium and CO_2 (see Formations 3, 5, and 6).

Identification.—Oxalic acid may be identified by giving off CO_2 and CO when heated with conc. H_2SO_4, and by giving a precipitate with $CaCl_2$ insoluble in acetic acid.

The following are the principal oxalates :—

Potassium Oxalate, $C_2O_4K_2.H_2O$, is a readily soluble salt finding some employment in photography. The **acid potassium oxalate,** C_2O_4HK, which is less soluble, is found in many plants, and forms with oxalic acid the **quadroxalate,** $C_2O_4HK.C_2O_4H_2.2H_2O$. The two latter salts are both sold as "salts of sorrel," or "salts of lemon," and are used in the removal of iron-stains. All these salts can be prepared by suitable neutralisation of the acid with potassium carbonate.

Sodium and Ammonium Oxalates are similarly prepared. **Calcium Oxalate,** $C_2O_4Ca.H_2O$, also obtainable anhydrous, is present in many plants, and, on account of its insolubility, serves for the estimation of calcium. **Ferrous Oxalate,** $C_2O_4Fe_2.H_2O$, is used as a developer in photography. **Antimony Oxalate** and the double oxalate of potash and antimony find some employment in dyeing. The silver salt, $Ag_2C_2O_4$, if quickly heated when dry, explodes.

Esters of Oxalic Acid.—Being di-basic, oxalic acid can produce two series of ethereal salts, acid and neutral respectively.

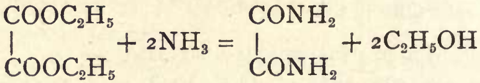
Methyl Hydrogen Oxalate and **Methyl Oxalate** are both solids, and are formed when oxalic acid acts upon methyl alcohol. Water saponifies them. The **ethyl oxalates** are liquids formed correspondingly from ethyl alcohol.

Ethyl Oxalate, or **Oxalic Ether,** $C_2O_2(OC_2H_5)_2$, is formed by the action of dry oxalic acid on alcohol.

†*Process.*—Heat together 120 grams of anhydrous oxalic acid and 80 grams absolute alcohol to 100° for 3 or 4 hours in a flask provided with a reflux condenser. Then pass in the *vapour* of 80 grams more alcohol while raising the temperature to 125°–130°.

Properties.—It is a colourless liquid, b.p. 186°, sp. gr. 1·0793 at $\frac{20^\circ}{4^\circ}$, and is readily hydrolysed by water.

Oxamide,  $\begin{array}{l}CONH_2\\ |\\ CONH_2\end{array}$, is produced when the last-named compound is treated with aqueous ammonia—



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + 2NH_3 = \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} + 2C_2H_5OH$$

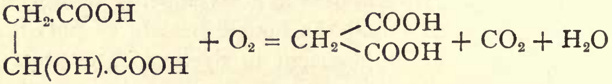
and also (2) when ammonium oxalate is heated—

$$C_2O_2(ONH_4)_2 = C_2O_2(NH_2)_2 + 2H_2O$$

(compare formation of acetamide from ethyl acetate and ammonium acetate, p. 182). Also notably (3) from cyanogen in aqueous solution, if a trace of aldehyde is present.

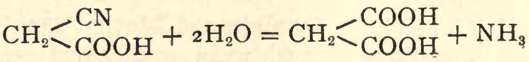
Properties.—It is a white crystalline solid, little soluble in water or alcohol. On heating with water to 200°, or with dilute acids, it re-forms ammonium oxalate.

Malonic Acid, $C_3H_4O_4 = CH_2(COOH)_2$, is found in beet-root juice, and is produced (1) by the slow oxidation of malic acid with potassium dichromate—



$$\begin{array}{l}CH_2.COOH\\ |\\ CH(OH).COOH\end{array} + O_2 = CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array} + CO_2 + H_2O$$

(2) It is best prepared *synthetically* from cyanacetic acid by saponification with either alkalis or acids; (cyanacetic acid is readily produced by acting upon chloracetic acid with KCN)—



$$CH_2\begin{array}{l}\diagup CN\\ \diagdown COOH\end{array} + 2H_2O = CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array} + NH_3$$

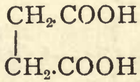
†*Process.*—100 grams of chloracetic acid, $CH_2Cl.COOH$, dissolved in 200 grams of water are neutralised with 75 grams of K_2CO_3, and the solution heated with 70 grams KCN. When the reaction is over, 100 grams KOH are added; the liquid is boiled till free from NH_3, then acidified with HCl, evaporated to dryness, and the acid extracted by ether, from which it can be obtained by evaporating off the solvent.

(3) It is also formed by the oxidation of several of the olefines.

Properties.—Malonic acid crystallises in triclinic tables, m.p. 132°–134°, and a little over this temperature decomposes *into acetic acid and* CO_2. It is readily soluble in water, alcohol, and ether. Its alkaline salts undergo electrolysis in strong solutions, with liberation of CO_2, CO, and O, but no hydrocarbon. If heated with acetic anhydride, it gives a reddish-yellow liquid with greenish fluorescence.

The *constitution* of malonic acid is shown (1) by its formation from cyanacetic acid, and (2) by its production when hydracrylic acid is gently oxidised. It forms acid and neutral esters, of which **ethyl malonate or malonic ether,** $CH_2(COOC_2H_5)_2$, is the most remarkable, and will be referred to later (see Appendix, p. 283).

Succinic Acids, $C_4H_6O_4$.—There are two isomeric acids with this general formula, viz. succinic acid and isosuccinic acid.

1. Succinic Acid,  $\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$, *ethylene dicarboxylic acid*, is very widely distributed in nature, being found in the lettuce, in various varieties of wormwood, in the poppy, celandine, and unripe grapes. It frequently occurs in urine, is present in the spleen of the ox, and is found in other animal substances. It is also found in amber and fossil wood; and the oldest method of preparing succinic acid is by the distillation of amber, hence its name (Lat. *succinum*, "amber").

Process.—Distil amber from a retort, heat the filtrate, filter through a moist filter-paper, and evaporate to the crystallising point. The yellow crystalline product is boiled with HNO_3, sp. gr.

1·32, to free it from traces of empyreumatic oils, and recrystallised from water.

Succinic acid is readily prepared (*2) by the reduction of malic acid, and of tartaric acid (monohydroxy- and dihydroxy-succinic acids), either by fermentation or hydriodic acid; *e.g.*—

$$C_2H_3(OH)(COOH)_2 + H_2 = C_2H_4(COOH)_2 + H_2O$$
$$C_2H_2(OH)_2(COOH)_2 + 4HI = C_2H_4(COOH)_2 + 2H_2O + 2I_2$$

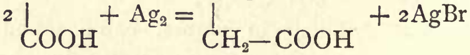
(3) A noteworthy synthetical formation of succinic acid occurs when ethylene dibromide is treated with KCN, and the resulting ethylene cyanide boiled with acids or alkalis—

$$\text{(i.)}\quad C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + {}_2KBr$$
$$\text{(ii.)}\quad C_2H_4(CN)_2 + 4H_2O = C_2H_4(COOH)_2 + 2NH_3$$

Ethylene chloride can also be employed.

†*Process.*—Boil an alcoholic solution of 100 grams of ethylene dibromide with 75 grams KCN till no further formation of KBr takes place, using a flask combined with a reflux condenser. Filter from the KBr, add 65–70 grams of KOH, and once more boil till the strong evolution of NH_3 ceases. Then cool the liquid, acidify with HCl, evaporate to dryness, and boil out the residue several times with alcohol. Distil off the alcohol, dissolve the crystalline residue in water, add animal charcoal, boil, and filter. Colourless crystals can then be obtained from the filtrate.

(4) Succinic acid is also produced when finely divided silver acts upon bromacetic acid—



$$2\begin{array}{l}CH_2Br\\ |\\ COOH\end{array} + Ag_2 = \begin{array}{l}CH_2\text{—}COOH\\ |\\ CH_2\text{—}COOH\end{array} + 2AgBr$$

(compare the formation of C_2H_6 from CH_3I, p. 43); and (5) is a product of the action of HNO_3 on many organic substances, such as fats, fatty acids, wax, etc.

Properties.—Succinic acid forms white or colourless crystals, which belong to the monoclinic system, sp. gr. 1·55, m.p. 185°. It boils at 235°, decomposing into its anhydride and water. It has a weakly acid taste, is readily soluble in water, less in alcohol, and still less in ether. It is a very stable substance, not being acted upon by HNO_3 or chlorine, although $KMnO_4$

in acid solution forms CO_2. On electrolysis, hydrogen is evolved at the negative, and CO_2 and C_2H_4 at the positive pole (see p. 54).

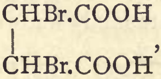
Constitution.—Since succinic acid can be prepared from ethylene cyanide, which is formed in its turn from ethylene bromide, it is evident that the acid contains the group $—CH_2.CH_2—$, and is best represented by the formula already assigned to it. This conclusion is confirmed by its formation from bromacetic acid by the method given. Since, too, ethylene can be built up from its elements, it is therefore evident that succinic acid can also be.

Identification.—Succinic acid is characterised by its irritating vapour when heated; by yielding a reddish precipitate with $FeCl_3$ in neutral solutions, which decomposes on addition of NH_4HO, giving a basic succinate; and by giving a precipitate with $BaCl_2$ when alcohol and NH_4HO are added (*difference from benzoic acid*).

Succinates.—The salts of succinic acid differ considerably in their solubility in water. The alkaline salts are readily soluble; the others are either almost or entirely insoluble.

Haloid Substitution Products of Succinic Acid.—Amongst the derivatives of succinic acid may be mentioned the mono- and di-brom-succinic acids, which are interesting as serving in the synthesis of malic acid and of tartaric acid respectively.

Mono-brom-succinic Acid, $C_2H_3Br(COOH)_2$, may be obtained by addition of hydrobromic acid to fumaric acid (p. 241); or by the action of 1½ parts bromine and 8 parts water upon 1 part succinic acid at 120°. It crystallises in colourless prisms, which melt at 160° and lose HBr. It forms malic acid when treated with moist silver oxide (see p. 249).

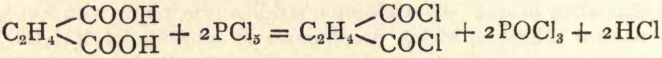
Di-brom-succinic Acid, 
$\begin{array}{l}CHBr.COOH\\ |\\ CHBr.COOH\end{array}$, may be formed from fumaric acid and bromine, or when bromine acts upon succinic acid—

$$C_2H_4(COOH)_2 + 2Br_2 = C_2H_2Br_2(COOH)_2 + 2HBr$$

†*Process.*—Heat 12 grams succinic acid, 33 grams bromine, and 12 grams of water in a closed tube to 160°–180° for six hours. The tube is allowed to cool, and the grey crystalline mass contained in it is recrystallised from hot water, being decolourised by the addition of purified animal charcoal to the solution and filtration.

It forms opaque crystals little soluble in cold water, and loses HBr at 200°, leaving brom-maleic acid. On boiling the silver salt with water, it yields tartaric acid (see p. 253).

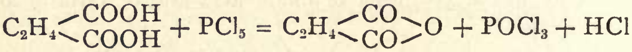
Succinyl Chloride, $C_2H_4(COCl)_2$ or $C_2H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$, is produced when succinic acid is treated with *two* molecular equivalents of PCl_5 (compare Acetyl chloride, p. 157)—



$$C_2H_4<\begin{matrix}COOH\\COOH\end{matrix} + 2PCl_5 = C_2H_4<\begin{matrix}COCl\\COCl\end{matrix} + 2POCl_3 + 2HCl$$

This substance is an oil, which solidifies at 0°, b.p. 190°–200°, sp. gr. 1·39. It behaves with water, alcohol, etc., as an acid chloride (compare Acetyl chloride); but in many of its reactions it acts as if possessing the second formula assigned to it.

Succinic Anhydride, $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>O$, is formed if the chloride is distilled with the acid, or if the acid is heated alone or with P_2O_5, or treated with *one* molecular equivalent of PCl_5—

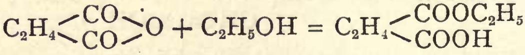


$$C_2H_4<\begin{matrix}COOH\\COOH\end{matrix} + PCl_5 = C_2H_4<\begin{matrix}CO\\CO\end{matrix}>O + POCl_3 + HCl$$

It crystallises in needles, m.p. 119°, b.p. 261°, and behaves in an analogous manner to acetic anhydride.

The student should note here *the formation of an acid anhydride from one molecule of an acid.*

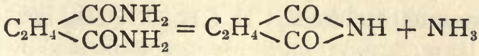
Succinic Esters can be produced by the general methods illustrated (p. 161). Thus succinic anhydride reacts with ethyl alcohol to form the only known acid ester—



$$C_2H_4<\begin{matrix}CO\\CO\end{matrix}>O + C_2H_5OH = C_2H_4<\begin{matrix}COOC_2H_5\\COOH\end{matrix}$$

and the normal esters are produced by the action of gaseous HCl on solutions of the acid in the alcohols.

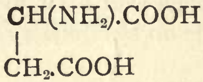
Succinamide, $C_2H_4(CONH_2)_2$, is a white powder formed from the ethyl ester by the action of aqueous ammonia (see Acetamide, p. 182); and when it is heated, a substance known as **Succinimide** is produced—



$$C_2H_4{<}\begin{matrix}CONH_2\\ CONH_2\end{matrix} = C_2H_4{<}\begin{matrix}CO\\ CO\end{matrix}{>}NH + NH_3$$

Succinimide is also formed when succinic anhydride is ignited in a current of NH_3, or when ammonium succinate is distilled (compare this reaction with that which occurs when ammonium acetate is distilled with NH_3, p. 182). It forms large efflorescent crystals, m.p. 126°, b.p. 288°, soluble in water and alcohol. It forms compounds with metals in which the imido (NH) hydrogen is replaced by them. *This acid character is characteristic of imides.*

Amido-succinic Acid, or **Aspartic Acid**—



$$\begin{array}{l}CH(NH_2).COOH\\ \vert\\ CH_2.COOH\end{array}$$

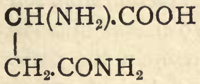
is found in beet-root juice after treatment with lime, in vinasse, and is a decomposition product of asparagine (see below) when boiled with alkalis or acids. It contains an asymmetric carbon atom, and the naturally occurring and best-known form is optically lævo-rotatory. It crystallises in plates, little soluble in water, insoluble in alcohol. When treated with HNO_2, aspartic acid yields *malic acid*—

$$C_2H_3(NH_2)(COOH)_2 + HNO_2 = C_2H_3(OH)(COOH)_2 + N_2 + H_2O$$

Being an amido acid, it forms salts both with acids and alkalis (compare Glycocoll, p. 184).

The synthetically formed acid is optically inactive.

Asparagine,



$$\begin{array}{l}CH(NH_2).COOH\\ \vert\\ CH_2.CONH_2\end{array}$$

, *amido-succinamic acid,* can also occur in three forms, the ordinary form being lævo-rotatory. It occurs in germinating seeds, in the juice of asparagus, of lettuce, in the young shoots of peas and beans, and other plants, from the juice of which it can be separated by crystallisation. It crystallises in prisms, is tasteless, readily soluble in water, not soluble in alcohol or ether. When boiled with alkalis or dilute acids it forms aspartic acid, and HNO_2 changes it into malic acid.

2. Iso-succinic Acid, $CH_3.CH:(COOH)_2$, *methyl malonic acid*, can be produced from α-chlor-propionic acid by formation of the cyanide and decomposition of that with alkalis. It cannot, however, be prepared from ethylidene bromide in that way, as ordinary succinic acid is produced.

Properties.—Isosuccinic acid forms colourless prisms or needles, which sublime at 100° in plates, melt at 130°, and, if heated more strongly, break up into propionic acid and CO_2 (compare with Oxalic, Malonic, and Succinic acids).

$$CH_3.CH.(COOH)_2 = CH_3.CH_2.COOH + CO_2$$

It gives no precipitate with $FeCl_3$ in neutral solutions, and does not yield ethylene on electrolysis (*differences from succinic acid*).

Adipic Acid, $C_6H_{10}O_4$, is noteworthy because it is a product of the oxidation of fats. It is formed from β-iodo-propionic acid by finely divided silver (see Succinic acid, Formation 5), and crystallises in prisms, m.p. 148°.

GENERAL REMARKS ON THE DICARBOXYLIC ACIDS.

The formation of these acids from the glycols, from hydroxy-fatty acids, and from haloid derivatives of paraffins or of fatty acids through the cyanides, have all been illustrated, and are general methods of production, while their formation from malonic ether (see Appendix, p. 283) is of special interest.

Properties.—They are crystallisable solids, generally volatile, soluble in water. The two classes of acids are differentiated on heating. Those which contain the carboxyl groups attached to one carbon atom do *not* yield anhydrides, but lose CO_2, and form a fatty acid; while those of which succinic acid is the type form anhydrides by *loss of water from one molecule* (*difference from fatty acids*).

UNSATURATED DICARBOXYLIC ACIDS.

Fumaric and Maleic Acids, $C_2H_2(COOH)_2$, contain two atoms less hydrogen than succinic acid, and are *physically* isomeric. When malic acid is distilled it loses H_2O, and fumaric acid remains behind, while maleic acid and its anhydride distil over—

$$C_2H_3(OH).(COOH)_2 = C_2H_2(COOH)_2 + H_2O$$

Fumaric acid is also formed by the action of KOH on bromsuccinic acid. Fumaric acid has a very acid taste, crystallises in small prisms, is almost insoluble in water, and melts at 200°, forming maleic anhydride. Maleic acid has a peculiar taste, crystallises in large prisms, is easily soluble in cold water, melts at 130°, and distils at 160°, forming the anhydride. If it is heated for some time to 130°, maleic acid changes into fumaric acid. Both acids yield acetylene on electrolysis (see p. 60).

SECTION V.

POLYHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

CHAPTER XXXII.

TRIHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

FEW of the trihydroxyl derivatives of the hydrocarbons are known, and by the rule which has already been given (p. 120) the first stable trihydric alcohol must contain at least three carbon atoms. The symmetrical trihydroxy-propane, $CH_2OH.CHOH.CH_2OH$, known as glycerol, is actually the first of the series, and this will be taken as typical.

It must not be forgotten, however, that, just as *derivatives* of the dihydric methylene and ethylidene alcohols exist, although they themselves are not known in the free state, so there are certain compounds which appear from their formation to be ethers of trihydric alcohols, in which the hydroxyl groups are all combined with one carbon atom. These substances are generally known as the **esters** of **ortho-acids.**

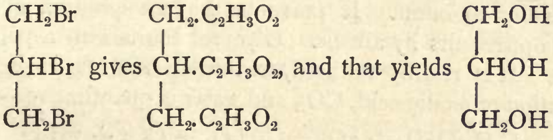
Thus formic acid appears to form the compound called "**ortho-formic acid,**" corresponding to $CH(OH)_3$; but it has not been isolated. On the other hand, its so-called esters, or, more properly speaking, its ethers, looking upon them as derived from a trihydric alcohol, are formed in the usual manner by the action of a trihaloid paraffin upon an alcoholate (compare Formation 2 of ether, p. 105). For example, **ethyl "orthoformate"** is formed thus—

$$CHCl_3 + 3C_2H_5ONa = CH(OC_2H_5)_3 + 3NaCl$$

and the corresponding ethane derivative, "**ethyl orthoacetate**," $CH_3.C(OC_2H_5)_3$, is similarly produced from the trichlor-ethane, $CH_3.CCl_3$.

Glycerol, or **Glycerin**, $C_3H_5(OH)_3$, *propenyl alcohol.*—Glycerin was discovered in the preparation of "lead plaster," formed by saponifying olive oil with lead oxide; and occurs combined with very many different acids in various natural fats and oils. Thus it is combined with butyric acid in butter fat, with palmitic acid in palm oil and lard, and with oleic acid in olive, lard, and almond oils, it is therefore a constant product of their saponification by whatever means that is effected. It exists in combination with phosphoric acid in the brain substance, and is a constant product of the alcoholic fermentation of sugar, and so is found in beer and wine.

Glycerol may be synthesised by methods identical in principle with those used and described for the mono- and di-hydric alcohols. Thus certain halogen derivatives of propane yield it by treatment with moist silver oxide, by formation of esters and saponification, or even by boiling with water; *e.g.* it can be obtained from tribrom-propane by the steps indicated, barium hydrate being employed to saponify the triacetate (triacetin)—



$$\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2Br \end{array} \text{ gives } \begin{array}{l} CH_2.C_2H_3O_2 \\ | \\ CH.C_2H_3O_2, \\ | \\ CH_2.C_2H_3O_2 \end{array} \text{ and that yields } \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Similarly, the trichlor-propane obtained from acetone yields it on heating with water to 180°—

$$CH_2Cl.CHCl.CH_2Cl + 3H_2O = CH_2OH.CHOH.CH_2OH + 3HCl$$

Manufacture.—Glycerin was originally manufactured by saponifying olive oil with lead oxide; the watery liquid remaining was freed from lead by means of H_2S and concentrated. It is now prepared by saponifying fats under pressure with *small* quantities of lime (2 to 3 per cent.), the liquid being then separated from the fatty matters, and concentrated.

In another process fats are heated with concentrated H_2SO_4

next boiled with water, and the acid liquid separated. The excess of acid is removed by neutralising with lime, and after the $CaSO_4$ has subsided the liquid is concentrated by evaporation.

Crude glycerin is purified by filtration through animal charcoal, and then concentrated in vacuum pans. To further purify this product, it may be distilled in a current of steam, or it may be crystallised.

Within the last few years many patents have been taken out for the recovery of glycerin from ordinary soap lyes, but these are too complex for description here.

Properties.—Glycerol is a colourless syrup, with a sweet taste, sp. gr. 1·2624 at $\frac{15^\circ}{15^\circ}$. It boils at 290° with partial decomposition, but can be distilled unchanged at diminished pressure, and also in a current of steam (see above). On cooling to 0° it solidifies to crystals, which melt at 20°. It is very hygroscopic, and can absorb more than half its own weight of water, is miscible with water or alcohol, but is not soluble in ether or chloroform.

Glycerol possesses antiseptic properties, and is noteworthy for its great solvent powers. For example, it dissolves NaOH, KOH, lead oxides, many sulphates and chlorides, and such salts as Na_2CO_3, alum, and lead acetate in considerable quantities, besides dissolving iodine, phosphorus, and sulphur in smaller amounts. It prevents the precipitation of ferric and copper salts by alkalis. Glycerol burns with a pale blue flame. It is readily oxidised, and when $KMnO_4$ is used, the formation of oxalic acid, CO_2, and water is quantitative—

$$C_3H_5(OH)_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O$$

Other oxidising agents yield, according to their strength, different products, including glycerose, glyceric acid, tartronic acid, racemic acid, CO_2, and other substances. If oxidised by PbO_2, and then bromine vapour, "glycerose" is produced, which apparently contains glyceric aldehyde.

When heated alone or with dehydrating agents, *e.g.* P_2O_5, or H_2SO_4, it yields acrolein (p. 210). Hydriodic acid or phosphorus and iodine form allyl iodide (p. 207), iso-propyl-iodide, etc.

Tests of Purity.—Glycerol finds considerable use in medicine and the arts, and the following tests are useful: If pure, it should give no precipitate with lead acetate. It should not give a precipitate with $AgNO_3$, nor a sensible precipitate with Fehling's solution, if heated with it for a few minutes to 100°. It should give no colour when heated with strong H_2SO_4, and very little with alkalis.

For the manufacture of "nitroglycerin," it is usual to test its purity by nitrating a sample under carefully fixed conditions. The purer the sample is, the sharper is the line of demarcation between the residual layer of acids and the "nitro-compound."

Identification.—On heating glycerol with concentrated H_2SO_4 or $KHSO_4$, the vapour of acrolein is evolved, known by its pungent odour. If the glycerol is in aqueous solution, saturate with $KHSO_4$, and then heat. If a borax bead is moistened with glycerol or its solution (if very weak, concentrate) and heated in a Bunsen flame, the green coloration due to boric acid will be observed (ammonium salts must be absent). If equal volumes of phenol, glycerol, and H_2SO_4 are mixed together and heated to 120°, then diluted with water and NH_4HO added, a crimson colour is obtained.

Glycerol, being an alcohol, can form both ethers and compound ethers or esters.

The former are of little importance, and can be obtained by ordinary methods; on the contrary, the esters, both of inorganic and organic acids, are important.

HALOID ESTERS OF GLYCEROL, OR CHLORHYDRINS.

When glycerol is treated with HCl, four different substances are formed in varying quantities, viz. two isomeric monochlorhydrins, and two dichlorhydrins, which are respectively—

1. $CH_2Cl.CH(OH).CH_2OH$
α or unsym. chlorhydrin
2. $CH_2(OH).CHCl.CH_2OH$
β or sym. chlorhydrin

and

3. $CH_2Cl.CHCl.CH_2OH$
α or unsym. dichlorhydrin
4. $CH_2Cl.CH(OH).CH_2Cl$
β or sym. dichlorhydrin

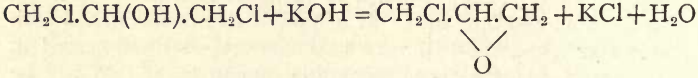
The β-chlorhydrin is also formed by the addition of HOCl to allyl alcohol; the α-dichlorhydrin by the action of sulphur chloride, S_2Cl_2, upon glycerol, and the β compound by the addition of HOCl to allyl chloride. They are all liquid substances. Trichlorhydrin, $CH_2Cl.CHCl.CH_2Cl$, trichlorpropane, or glyceryl trichloride is obtained by the action of PCl_5 upon both the dichlorhydrins—

$$CH_2Cl.CHCl.CH_2OH + PCl_5 = CH_2Cl.CHCl.CH_2Cl + POCl_3 + HCl$$

It is a liquid, b.p. 158°, and reverts to glycerol when boiled with twenty times its own volume of water.

GLYCIDE COMPOUNDS.

When the dichlorhydrins are treated with caustic potash or soda, they lose HCl and form **epi-chlorhydrin,** or **glycide chloride**—



$$CH_2Cl.CH(OH).CH_2Cl + KOH = CH_2Cl.\underbrace{CH.CH_2}_{O} + KCl + H_2O$$

which is a mobile liquid with a chloroform-like taste and smell, b.p. 116·6° (cor.), sp. gr. 1·203 at $\frac{0^\circ}{4^\circ}$. It is nearly insoluble in water, which at 100° converts it into α-chlorhydrin. Like ethylene oxide (see p. 219), it unites with $NaHSO_3$, and the chlorine atom is replaceable by OH, or by acid radicles, with the respective formation of glycide alcohol, or glycide esters.

GLYCEROL ESTERS OF NITRIC ACID.

"**Nitro-glycerin,**" or **Glyceryl Trinitrate,** $C_3H_5(NO_3)_3$, *trinitrin* is the principal ester of glycerol and nitric acid, and is not, as its name would indicate, a "nitro-compound," but a real salt of nitric acid, prepared by the action of strong HNO_3 upon glycerol, concentrated H_2SO_4 being used as a dehydrating agent—

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(ONO_2)_3 + 3H_2O$$

Manufacture.—About 2 parts (by weight) of HNO_3 sp. gr. 1·5, and 4 parts of H_2SO_4 sp. gr. 1·84, are thoroughly mixed and cooled. About 0·5 part of glycerol is then injected into the mixture in the form of a fine spray, and becomes immediately nitrated, while considerable rise of temperature occurs. The mixture is kept in constant agitation, and the temperature carefully kept below 27°

while the reaction proceeds. When it is over, the mixture is allowed to stand and separate, and the nitro-glyerin is drawn off from the top and well washed, first with water and then with alkali, till the wash-water is alkaline to test paper. It is then stored, ready for conversion into dynamite. **Dynamite** is a mixture of nitro-glycerin and kieselguhr, the latter being a highly silicious infusorial earth which, after calcining, will absorb three or four times its weight of the nitro-compound, and retain it under pressure. Dynamite finds much more employment than nitro-glycerin, because it can be stored and handled with so much greater safety.

Properties.—Nitro-glycerin is a heavy, oily, and, if pure, colourless liquid, sp. gr. 1·60 at 15°, which, *when quite pure*, will keep unchanged for a very long time. Traces of impurities, and sunlight, will start its decomposition, glyceric, oxalic, and nitrous acids being formed. It is slightly soluble in water, very soluble in alcohol, ether, and chloroform. It solidifies on cooling, forming needles which melt at about 11°. It has no smell, has a sweet taste, and is poisonous, small quantities producing vertigo and headache—even handling it will produce these symptoms. Reducing agents, *e.g.* $(NH_4)_2S$ and HI, reduce it to glycerol. Potash decomposes, but does not saponify it in the ordinary manner, as HNO_2 is formed—

$$C_3H_5(ONO_2)_3 + 5KOH = KNO_3 + 2KNO_2 + \underset{\text{Potassium formate}}{H.COOK}$$
$$+ \underset{\text{Potassium acetate}}{CH_3.COOK} + 3H_2O$$

Nitro-glycerin is a highly explosive compound, exploding with great violence when exposed to shock, as in detonation, or when heated. It contains more than enough oxygen in itself for its own combustion; the following equation expresses the reaction :—

$$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O$$

The liability to explode on handling is much less when it is used in the form of *dynamite*, or when it is transformed into *blasting gelatin* or *cordite*, which are combinations of it with guncotton, camphor, etc.

OXIDATION PRODUCTS OF GLYCEROL.

Since the three-carbon alcohol, glycerol, contains two primary alcoholic groups, it might be expected to give by oxidation two aldehydes and two acids, containing one or two aldehydic or carboxylic groups. The same might be predicted of other similar trihydric alcohols.

Little is known of the aldehydes (see Glycerose, p. 244); but the mono- and di-basic acids derived from glycerol are well known.

The monobasic acids, which contain *two* alcoholic groups, *may* be looked upon as hydroxy-acids derived from those of the *lactic series* (see formation of Glyceric acid, below); and the dibasic acids, which contain *one* alcoholic group, as hydroxy-substitution derivatives of the acids of the malonic series (compare formation of Tartronic and Malic acids, p. 249).

The three acids named will be the only ones considered.

DIHYDROXY-CARBOXYLIC ACIDS.

The first *stable* dihydroxy-carboxylic acid is glyceric acid, for though in some reactions glyoxylic acid (p. 223) appears to be dihydroxy-acetic acid, in others it acts as an aldehyde.

Glyceric Acid, $CH_2(OH).CH(OH).COOH$, *dihydroxy-propionic acid*, is formed (1) when glycerol, mixed with an equal quantity of water, is carefully oxidised by HNO_3, sp. gr. 1·5—

$$CH_2(OH).CH(OH).CH_2OH + O_2 \\ = CH_2(OH).CH(OH).COOH + H_2O$$

also (2) by acting with silver oxide upon β-chlor-lactic acid.

$$CH_2Cl.CH(OH).COOH + AgOH \\ = CH_2(OH).CH(OH).COOH + AgCl$$

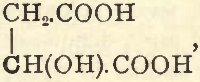
It forms an uncrystallisable syrup, readily soluble in water, is optically inactive, but is evidently a mixture of acids of optically different properties. On heating to 105° for some time, it forms an anhydride. Its salts crystallise well.

Hydroxy-Dicarboxylic Acids.

Tartronic Acid, $CH(OH).(COOH)_2$, *hydroxy-malonic acid*, is, amongst other methods, produced (1) by oxidising glycerol with potassium permanganate—

$$CH(OH).(CH_2OH)_2 + 2O_2 = CH(OH).(COOH)_2 + 2H_2O$$

also (2) from brom-malonic acid, $CHBr(COOH)_2$, by the action of silver hydroxide. It is a transparent solid, which crystallises in large prisms, is readily soluble in water, and melts at 184°, forming *glycolide* and CO_2.

Malic Acid,  $\begin{array}{l} CH_2.COOH \\ | \\ CH(OH).COOH \end{array}$, *hydroxy-succinic acid*, is very widely distributed in the vegetable kingdom, *e.g.* it is found free, mixed with other acids, in such fruits as red and white currants, raspberries, blackberries, morella cherries, unripe apples, and the berries of the mountain ash, and is present as the acid potassium salt in sweet cherries and ordinary rhubarb. It is also a constituent of the "yolk" which is found in such large quantities on wool.

Malic acid is ordinarily and most easily prepared from the juice of *unripe* mountain-ash berries.

Process.—Filter the juice, almost neutralise it with lime, and boil for some time. Remove the white calcium malate which separates, with a spoon, and when no more falls out, cool the liquid, when a further amount separates. Wash with cold water, add it to boiling dilute HNO_3 (1 acid : 10 water) till no more dissolves. Allow to cool, and recrystallise the acid calcium malate which separates, from water. To obtain the free acid, dissolve the acid malate in water, precipitate it by lead acetate, wash, and decompose the lead compound by H_2S. From the syrupy solution the acid will crystallise out.

Malic acid can be synthetically prepared (1) by the action of moist silver oxide on monobrom-succinic acid (compare formation of lactic acid from α-chlor-propionic acid)—

$$C_2H_3Br(COOH)_2 + AgOH = C_2H_3(OH).(COOH)_2 + AgBr$$

This reaction yields it in an inactive form.

A dextro-rotatory variety is produced (2) by partial reduction of tartaric acid with hydriodic acid—

$$C_2H_2(OH)_2(COOH)_2 + 2HI = C_2H_3OH(COOH)_2 + H_2O + I_2$$

This form possesses opposite optical properties to that found in plants, which is lævo-gyrate; but (3) if malic acid is formed by the action of HNO_2 on asparagine (see p. 239), its properties are identical with those of the natural acid.

Properties.—Malic acid exists in three optically distinct varieties, viz. the dextro- and lævo-rotatory, and the inactive forms. Of these the best known is the ordinary or lævo-rotatory variety. It forms colourless needles, sp. gr. 1·559, which have an acid taste, deliquesce in moist air, and melt at 100°. It is very soluble in water, forming solutions which when dilute are lævo-rotatory, and when concentrated dextro-rotatory; the addition of H_2SO_4 renders the latter solutions lævo-rotatory. It yields, on heating to temperatures from 140° to 200°, varying amounts of fumaric anhydride and maleic acid (p. 241). Malic acid is *reduced* by concentrated HI to succinic acid. Certain *schizomycetes* also reduce it to succinic and less complex acids. It prevents the precipitation of salts of copper and iron by alkalis.

Constitution.—The constitution of malic acid follows from its production from monobrom-succinic acid, which shows it to be hydroxy-succinic acid.

Identification.—There are no very characteristic qualitative tests; however, in neutral solutions it does not give a precipitate with $CaCl_2$, unless the solution is very strong, or alcohol is present (*distinction from tartaric and oxalic acids*). The calcium salt is soluble in NH_4HO (*difference from citric acid*). Lead acetate gives a white precipitate in solutions of malic acid, best if the solution is neutralised by NH_4HO. On heating the precipitate it partly dissolves, the rest fuses together; it is soluble in dilute acetic acid at 60° (*difference from citrate and tartrate*).

Salts.—The acid salts of the alkalis crystallise well, the normal salts with difficulty, and the salts of many other metals are non-crystallisable. The ammonium, calcium, and lead salts are amongst the most characteristic.

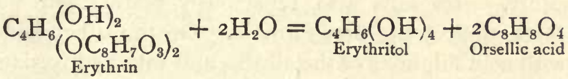
CHAPTER XXXIII.

TETRA-HYDRIC ALCOHOLS AND THEIR DERIVATIVES.

ALCOHOLS.

THE first stable alcohol which contains four hydroxyl groups also contains four carbon atoms, and is a tetra-hydroxy-butane.

Erythritol, $C_4H_{10}O_4 = CH_2(OH).CH(OH).CH(OH).CH_2OH$, or **Erythrite.** It is found free in the alga *Protococcus vulgaris*, and in erythrin—a substance which occurs in orchella weed, a lichen of the species *Rocella*, largely used in preparing the dye orchill. This substance readily yields it on decomposition with milk of lime—



$$\underset{\text{Erythrin}}{C_4H_6\begin{matrix}(OH)_2\\(OC_8H_7O_3)_2\end{matrix}} + 2H_2O = \underset{\text{Erythritol}}{C_4H_6(OH)_4} + \underset{\text{Orsellic acid}}{2C_8H_8O_4}$$

Properties.—Erythritol crystallises in large quadratic crystals, m.p. 112°, b.p. 330°, and sp. gr. 1·45. It has a sweet taste, and is optically inactive, although it contains two asymmetric carbon atoms, is very soluble in water, little in alcohol, and insoluble in ether. It does not reduce copper salts, and is not fermented by yeast. It yields, on oxidation by HNO_3, an aldehyde-like substance, and oxalic and tartaric acids.

TETRA-HYDRIC ACIDS.

Since erythritol contains two primary alcoholic groups, it can yield, on suitable oxidation, two different acids—one monobasic, erythric acid; the other dibasic, tartaric acid.

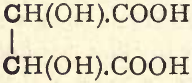
The trihydroxy-carboxylic acid, **erythric acid,** $CH_2OH.[CH(OH)]_2.COOH$, is a deliquescent substance, formed by oxidising erythritol by means of platinum black.

DIHYDROXY-DICARBOXYLIC ACIDS.

Mesoxalic Acid, $C_3H_4O_6$

$$\left.\begin{matrix}\text{Tartaric Acid}\\\text{Racemic Acid}\end{matrix}\right\} C_4H_6O_6$$

Mesoxalic Acid, $C_3H_2O_5.H_2O = C(OH)_2.(COOH)_2$, *di-hydroxy-malonic acid*, the first member of the series, is not derived from a four-carbon alcohol, and is therefore remarkable as containing *two hydroxyl groups attached to one carbon atom* (see p. 78), this unusual property of a carbon atom evidently being due to the influence upon it of the two carboxyl groups. Frequently, however, it behaves as if it were a ketonic acid, $CO(COOH)_2.H_2O$, several reactions being best explicable on such an assumption. (1) Mesoxalic acid is frequently prepared by heating alloxan, an oxidation product of uric acid, with baryta water. (2) It can also be formed by boiling dibrom-malonic acid, $CBr_2(COOH)_2$, with baryta water; hence its constitution. Mesoxalic acid forms very deliquescent crystals, which melt at 115°–120°, and do not lose water at that temperature. Its salts also tenaciously retain their water. These facts support the first formula. On the other hand, it unites with acid sulphites of the alkalis, and with hydroxylamine to form ketone-like derivatives, and also, like a ketone, yields, on reduction, tartronic acid (p. 249), which contains a secondary alcoholic group.

Tartaric Acids, $C_4H_6O_6 =$  $\begin{array}{l}CH(OH).COOH\\ |\\ CH(OH).COOH\end{array}$, *di-hydroxy succinic acids.*

There are *four* different acids known, all of which may be represented by the above constitutional formula.

1. Ordinary tartaric acid, the solutions of which rotate a ray of polarised light to the right;

2. Lævo- or anti-tartaric acid, which is lævo-gyrate;

3. Racemic acid, which is optically inactive, but can be split up into the two former acids; and

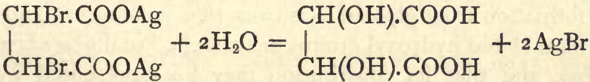
4. Para-tartaric acid, which is also optically inactive, but cannot be divided into the two active varieties.

1. **Dextro-tartaric Acid,** *ordinary tartaric acid*, is very widely distributed in nature, both in the free and the combined condition, the acid potassium tartrate being especially common. Thus it is found in grape juice, from which it is deposited during fermentation as "argol," which

is acid tartrate of potassium, mixed with some calcium tartrate and some salts of racemic acid. It also occurs in mountain-ash berries, mulberries, pine-apples, and in many plants.

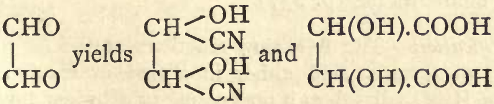
Manufacture.—Tartaric acid is prepared commercially from "argol," which, when recrystallised, is termed "tartar," and if still further purified forms "cream of tartar," or "cream." The tartar is added gradually to boiling water which contains whiting in suspension, until the whiting is entirely used up; then sufficient calcium sulphate is added to decompose any normal potassium tartrate remaining, and the whole is boiled for two hours. Calcium tartrate separates as a dense crystalline precipitate, is filtered off, and washed. It is then decomposed by dilute H_2SO_4, filtered from gypsum, concentrated in leaden pans, and then allowed to crystallise. The crystals are dried in a centrifugal machine, dissolved in water, and decolourised by means of purified animal charcoal; after filtration a little H_2SO_4 is added, and the liquid concentrated to the crystallising point in lead-lined vessels. The sulphuric acid causes a finer yield of crystals. These, however, contain small quantities of lead and sulphuric acid, and for pharmaceutical purposes require further recrystallisation from water.

Besides being obtained from argol, tartaric acid is formed (1) by the oxidation of dextrose, cane-sugar, milk-sugar, and other carbo-hydrates. (2) A noteworthy production of tartaric acid occurs when the silver salt of dibrom-succinic acid is boiled with water—



$$\begin{array}{l}\mathrm{CHBr.COOAg}\\ |\\ \mathrm{CHBr.COOAg}\end{array} + 2H_2O = \begin{array}{l}\mathrm{CH(OH).COOH}\\ |\\ \mathrm{CH(OH).COOH}\end{array} + 2AgBr$$

Another interesting synthesis (3) is that in which glyoxal is boiled with HCN and HCl—



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array}\ \text{yields}\ \begin{array}{l}\mathrm{CH}<^{\mathrm{OH}}_{\mathrm{CN}}\\ |\\ \mathrm{CH}<^{\mathrm{OH}}_{\mathrm{CN}}\end{array}\ \text{and}\ \begin{array}{l}\mathrm{CH(OH).COOH}\\ |\\ \mathrm{CH(OH).COOH}\end{array}$$

Racemic acid (mixed in formation (2) with inactive tartaric acid) is really the product of the last two reactions; but it will be shown (p. 257) that racemic acid can be readily split up into equal portions of the dextro- and lævo-rotatory varieties of tartaric acid.

Properties.—Tartaric acid crystallises in transparent monoclinic prisms, sp. gr. 1·7594 at $\frac{7^\circ}{4^\circ}$, m.p. 172°. These are luminous in the dark, if rubbed. Tartaric acid has a pure acid taste, is very soluble in water, less so in alcohol, and almost insoluble in ether. Its aqueous solutions are dextrorotatory.

When heated, tartaric acid melts at about 135°, and passes partly into amorphous *meta-tartaric acid;* on further heating, *ditartaric* or *tartralic acid* is formed; and finally *tartrelic acid* and *tartaric anhydride* are produced. Dry distillation yields, among other products, pyro-racemic (pyruvic acid) (p. 229) and pyro-tartaric acid. Strong oxidising agents form CO_2 and formic acid; weaker oxidising reagents produce hydroxymalonic acid. Hydriodic acid reduces it successively to malic and succinic acids.

Tartaric acid prevents the precipitation by alkalis of many metallic hydrates.

Uses.—Tartaric acid finds employment in dyeing and printing operations, in certain photographic processes, and in the manufacture of baking-powders, seidlitz powders, and effervescing drinks.

Constitution.—Tartaric acid is clearly proved, by its formation from dibrom-succinic acid, to be a dihydroxy-succinic acid. Its formation from glyoxal confirms this conclusion, and also shows that the hydroxyl groups are attached to different carbon atoms, and that its constitution may be represented by the formula given to it on p. 252. As, too, tartaric acid can be formed from succinic acid, it is clearly possible to build it up from its elements (see p. 237).

Identification.—The following reactions are useful for the recognition of tartaric acid either in a free or combined state: 1. Strong H_2SO_4 dissolves it on heating to a brown liquid, which rapidly blackens, and evolves CO_2 and SO_2. 2. Potassium acetate yields with the acid a crystalline precipitate of the acid-tartrate of potassium. In dilute solutions this only appears after some time; the addition of alcohol, and vigorous shaking, hasten its appearance. A neutral tartrate does not give this reaction until after the addition of some acid, *e.g.* acetic acid. Boric acid also prevents it, in which case use potassium fluoride and acetic acid instead of potassium acetate. 3. Normal tartrates give with $CaCl_2$ a white precipitate of calcium tartrate, which is soluble in cold NaOH or KOH solution (*difference from citrates and oxalates*). From these solutions it separates on boiling as a gelatinous precipitate, which slowly re-dissolves on cooling. 4. A solution of the acid gives no precipitate with $AgNO_3$; a neutral alkaline salt, however, gives a precipitate of silver tartrate, which is soluble in excess and in ammonia. On gently warming, these solutions yield a precipitate or mirror of metallic silver. 5. If to a solution of tartaric acid, or a slightly acid solution of its salts, a drop or two of NaClO solution is added, then one or two drops of $FeSO_4$ solution, and an excess of alkali, a beautiful violet liquid is obtained (*distinction from citric acid*).

Salts of Tartaric Acid.—Being dibasic, tartaric acid forms normal and acid salts; but it also forms so-called basic salts, due to metals replacing its alcoholic hydrogen. The salts, like the acid, are dextro-gyrate.

Acid Potassium Tartrate, $KC_4H_5O_6$, "cream of tartar," can be prepared by suitable purification of argol, or may be precipitated from a solution of the neutral tartrate by the addition of dilute HCl. It has a sour taste, and forms rhombic crystals.

Normal Potassium Tartrate, $2K_2C_4H_4O_6.H_2O$, forms monoclinic prisms, and is obtained by neutralising cream of tartar with K_2CO_3.

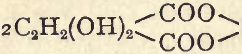
Acid and Normal Sodium Tartrates have little importance.

Potassium Sodium Tartrate, $KNaC_4H_4O_6.4H_2O$, known as "Seignette's salt" or "Rochelle salt," is prepared by neutralising cream of tartar with Na_2CO_3, and forms rhombic prisms; it is used in medicine as an aperient.

Calcium Tartrate, $CaC_4H_4O_6.4H_2O$, present in grapes and senna leaves, is obtained when a neutral tartrate solution is precipitated by $CaCl_2$ solution.

Lead Tartrate, $PbC_4H_4O_6$, is formed when tartaric acid is added to a solution of a lead salt. It is a crystalline powder, difficultly soluble in water. Its ammoniacal solution on boiling yields the basic salt $C_2H_2(O_2Pb).(COO)_2Pb.H_2O$.

Potassium Antimonious Tartrate, *tartar emetic,*



$2C_2H_2(OH)_2{<}{\scriptstyle\begin{matrix}COO\\COO\end{matrix}}{>}Sb.OK + H_2O$.—This substance is prepared by boiling a solution of cream of tartar with antimony trioxide and allowing the solution to crystallise. It forms efflorescent rhombic crystals, which, on heating, lose water, and form the compound $KSb'''C_4H_2O_6$. Tartar emetic is used as a sudorific and as an emetic.

Tartar emetic is not a true salt of tartaric acid, but is really the potassium salt of a conjugated acid formed from tartaric acid and SbO'', and does not give the ordinary reactions of tartrates.

2. **Lævo-tartaric Acid,** *antitartaric acid,* is obtained from racemic acid by the process described below. It is chemically similar in most of its properties to ordinary tartaric acid. It, however, crystallises in forms which are like the reflected images of those in which tartaric acid crystallises, and it differs from that acid in being lævo-rotatory. The salts of this acid differ similarly from those of tartaric acid.

3. **Racemic Acid,** *paratartaric acid,* remains in the mother liquor from which cream of tartar is crystallised, and can be obtained from that either as the calcium or sodium-ammonium salt. It is produced (1) with liberation of heat when equal weights of dextro- and lævo-tartaric acids are mixed in solution. It is also formed (2) by the oxidation of milk-sugar, cane-sugar, etc., with HNO_3; and (3) by heating tartaric acid with a little water to 175° for 30 hours.

Properties.—Racemic acid crystallises with 1 mol. of water, in prisms belonging to the tri-clinic system. These effloresce on exposure to air, and lose water at 100°. Racemic acid is optically inactive, and $CaSO_4$ gives a precipitate in solutions of it, which is insoluble in NH_4HO (*difference from tartaric acid*). *It gives the same decomposition products as tartaric acid.*

When a solution of ammonium sodium racemate is allowed to crystallise, two kinds of hemihedral crystals are deposited, the difference between which is the same as that between an object and its reflection in a mirror. If these are separated mechanically and decomposed by H_2SO_4, solutions of the dextro- and lævo-rotatory tartaric acids are obtained.

4. **Inactive Tartaric Acid**, *meso-tartaric acid*, is formed along with racemic acid from silver dibrom-succinate, by the oxidation of glycerol and of erythrite by HNO_3, and also by heating tartaric acid for two days with a little water to 165°; since its acid potassium salt is very soluble, it can be separated by means of that from the remaining tartaric acid. It crystallises in prisms with one molecule of water, and can be turned into racemic acid by heating with water to 175°. (Note this change and compare it with the formation of Racemic acid.)

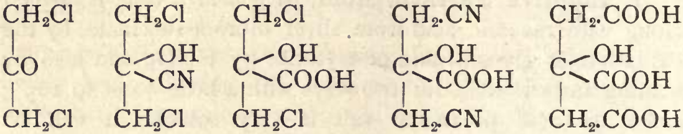
HYDROXY-TRICARBOXYLIC ACIDS.

The most important of this class is

Citric Acid, $C_3H_4(OH)(COOH)_3.H_2O$, or *hydroxy-tricarballylic acid*, which is found in many plants: thus free and alone, in lemons, oranges, sloes, and cranberries; along with malic acid in red currants, gooseberries, raspberries, and cherries; and mixed with malic and tartaric acids in mountain-ash berries. It is also found as the potassium and calcium salts in the juice of the lettuce and in the tobacco plant. The main source of citric acid is the juice of the lemon, although considerable quantities can be obtained from the lime and bergamot.

Manufacture.—Lemon juice is boiled with a slight excess of whiting, and the precipitated calcium citrate is filtered off and washed. The citrate is then decomposed by H_2SO_4, sp. gr. 1·7, the gypsum is filtered off, the liquid concentrated, and afterwards cooled with continual agitation. The crystals of citric acid are drained, then dissolved in water, decolourised with animal charcoal, and once more allowed to crystallise in leaden pans. As the crystals so obtained always contain a trace of lead, they require further purification if required for medicinal purposes.

Citric acid is synthetically obtained from symmetrical dichlor-acetone (i.), which yields by treatment with HCN dichlor-hydroxy-butyronitrile (ii.), which decomposed by HCl gives the corresponding acid (iii.). The potassium salt of the acid heated with KCN gives a dinitrile (iv.), which heated with HCl gives citric acid (v.)—



(i.) (ii.) (iii.) (iv.) (v.)

Properties.—Citric acid has a pleasant, sour taste, and crystallises with one molecule of water in transparent rhombic prisms, sp. gr. 1·54. It is very soluble in water and alcohol, but little so in ether, and its solutions are optically inactive. The crystals melt at 100°, and lose their water of crystallisation at about 130°, forming the anhydrous acid, which melts at 153°, and if heated to 175° decomposes into water and aconitic acid, $C_3H_3(COOH)_3$, a reaction which is analogous to the formation of acrylic, and of maleic and fumaric acids, from hydracrylic and malic acids respectively. On fusion with caustic potash, acetic and oxalic acids are formed, while its oxidation products vary with the agent employed. On reduction, citric acid yields **tricarballylic acid,** $C_3H_5(COOH)_3$, a tri-basic acid which can also be formed from glyceryl bromide, $C_3H_5Br_3$, by heating it with KCN and decomposing the tricyanide with potash.

Identification.—Citric acid resembles tartaric acid in some reactions, but differs from it by giving no smell of burnt sugar when heated, although very pungent acid fumes are evolved; it also darkens very much less after heating with conc. H_2SO_4. Neutral solutions of citrates give a precipitate with $CaCl_2$ only after long standing or when the solution is boiled (*difference from tartaric acid*), and the precipitate is insoluble (or almost so) in caustic alkalis (calcium tartrate is soluble). Citrates give a mirror with ammoniacal $AgNO_3$ much less readily than tartrates.

CHAPTER XXXIV.

PENTA- AND HEXA-HYDRIC ALCOHOLS.

PENTA-HYDRIC ALCOHOLS AND THEIR DERIVATIVES.

Arabitol, or **Arabite,** $CH_2(OH).(CHOH)_3.CH_2OH$(?), is probably a *penta-hydroxy-pentane*, and first of the series. It is obtained by the reduction of the aldehyde arabinose by sodium amalgam. It crystallises in prisms, m.p. 102°, is very soluble in water and hot alcohol. It has a sweet taste, and does not reduce Fehling's solution.

Arabinose, $CH_2(OH).(CHOH)_3.CHO$, is the aldehyde of the preceding alcohol, and has many properties analogous to the glucoses. It is not known in nature, but is formed by oxidising gum arabic, gum tragacanth, and other gums with HNO_3. It crystallises in rhombic prisms, m.p. 160°. They have a sweet taste, and are slightly soluble in water, the solution being dextro-rotatory. Arabinose reduces Fehling's solution, but is not fermentable by yeast; when oxidised by HNO_3, or bromine water, it produces the corresponding monobasic acid, **arabonic acid,** $C_5H_{10}O_6$, which is not known in a free condition, though its salts are known.

HEXA-HYDRIC ALCOHOLS AND THEIR DERIVATIVES.

This series include the following groups of substances :—

1. The alcohols, $C_6H_{14}O_6$, mannitol, dulcitol, and sorbitol.
2. Acids derived from them, which are not of importance to an elementary student.
3. The aldehyde and ketone derivatives; to which belong the **carbohydrates,** *i.e.* the sugars, starches, etc.

1. THE ALCOHOLS.

Mannitol, or **Mannite,** $CH_2(OH).(CHOH)_4.CH_2OH$, formerly termed manna sugar, is present to the extent of 30–60 per cent. in manna, which is the dried sap of the manna ash, and is prepared from that by extracting with alcohol and crystallising the product. It also is found in many plants, such as celery, olives, and sugar-cane, and in urine in special circumstances. It is produced in the viscous fermentation of sugar, and is formed artificially by the reduction of levulose or of dextrose by means of sodium amalgam—

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$$

Properties.—Mannitol crystallises in needles or prisms, m.p. 165°, sp. gr. 1·5, which have a sweet taste, are very soluble in water, slightly so in alcohol, and insoluble in ether. Aqueous solutions of mannitol are inactive, but addition of borax renders them dextro-rotatory. Mannitol is *not* fermentable by yeast. It loses water when heated to about 200°, forming the anhydride mannitan. It does *not* reduce Fehling's solution or $AgNO_3$. Careful oxidation yields mannose and levulose; oxidised with nitric acid, it yields saccharic acid and oxalic acid. It hinders the precipitation of iron and copper salts by alkalis. Hydriodic acid reduces it to secondary hexyl iodide. Being an alcohol, mannitol can form esters with both inorganic and organic acids; thus it forms a hexacetate and a hexa-nitrate, the latter being a highly explosive compound. These compounds show the presence in it of *six* hydroxyl groups.

Besides the dextro-gyrate form of mannitol, others are known which are lævo-rotatory, and inactive respectively.

Dulcitol, or **Dulcite,** $C_6H_{14}O_6$, *melampyrin,* isomeric with mannitol, is found in Madagascar manna, and prepared from it by recrystallisation. Galactose and milk sugar yield it when reduced by means of sodium amalgam.

Properties.—Dulcitol is less sweet than mannitol, and forms glittering prisms, m.p. 189°, sp. gr. 1·4. It is less soluble in water than mannitol, is almost insoluble in alcohol, and insoluble in ether. It does not ferment, and does not reduce Fehling's solution. HNO_3 oxidises it to mucic acid and oxalic acid. On heating, it forms the anhydride dulcitan. Dulcite yields with hydriodic acid secondary hexyl iodide, and also forms a hexacetate and a hexa-nitrate.

Sorbitol, $C_6H_{14}O_6$, *sorbite,* another isomer, from mountain-ash berries, is also reduced to secondary hexyl iodide by HI.

The reduction of these bodies to secondary hexyl

iodide shows them, and therefore the sugars derived from them, to be derivatives of normal hexane.

OXIDATION PRODUCTS OF THE HEXA-HYDRIC ALCOHOLS.

The alcohols just studied give rise by oxidation to **aldehyde-alcohols** and **ketone-alcohols**, forming the bodies known as the **hexoses** or **glucoses**; these latter in their turn yield di-, tri-, and poly-saccharides by elimination of water.

Besides these, the alcohols yield monobasic and dibasic acids.

In consequence of the alcohols, aldehydes, and acids containing asymmetric carbon atoms, *each of them can occur in three optically different varieties*—the dextro-, lævo-, and non-rotatory forms (p. 100). These forms are designated by the letters *d*, *l*, and *i* respectively, which refer, in the cases of the alcohols and acids, *not to their own rotation*, *but to that of the aldehydes to which they are related.* Each of these bodies also contains more than one asymmetric carbon atom; the total number of isomers is much increased on that account, but the reason for this cannot be discussed here.

The following table will help the student to understand the relationships between the different groups.

The names in black type are those of substances specially discussed in the text. It is convenient to study the acids before the carbohydrates, so as to keep the relationships of the latter clearly in view.

1. Alcohols	$C_6H_{14}O_6$	**Mannitols**	**Dulcitols**	**Sorbitols**
2. Monobasic acids ...	$C_5H_{11}O_5COOH$	Mannonic acid	Lactonic acid	Gluconic acid
3. Dibasic acids	$C_4H_8O_4(COOH)_2$	Manno-saccharic acid	**Mucic acid**	**Saccharic acid**
4. Carbo-hydrates :—				
(1) Saccharides—				
(*a*) Aldehyde alcohols or aldoses	$C_6H_{12}O_6$	Mannoses	Galactoses	**Glucoses** (dextrose)
(*b*) Ketone alcohols or ketoses	$C_6H_{12}O_6$	**Fructoses** (levulose)		Sorbinose
(2) Disaccharides (anhydrides of the saccharides)	$C_{12}H_{22}O_{11}$	**Cane-sugar** from glucose and levulose **Milk-sugar** ,, dextrose and galactose **Maltose** ,, dextrose		
(3) Polysaccharides ...	$(C_6H_{10}O_5)_n$	**Starch** **Dextrin** **Cellulose**		

2. ACIDS.

The two following acids correspond to sorbitol and glucose.

Gluconic Acid, $CH_2(OH).(CHOH)_4COOH$, can be prepared from cane-sugar, maltose, starch, glucose, and other carbohydrates by oxidising them with bromine water and silver oxide. The acid, liberated from the silver salt by H_2S, forms an uncrystallisable syrup, which is soluble in water, insoluble in alcohol. Its solutions are dextro-rotatory. When carefully oxidised with HNO_3, it yields the corresponding dibasic saccharic acid.

Saccharic Acid, $COOH.(CHOH)_4COOH$, is produced by the oxidation of gluconic acid by HNO_3 or by chlorine water. It is also formed by the oxidation of dextrose, cane-sugar, starch, and other carbohydrates by HNO_3, sp. gr. 1·15. It is a brittle, amorphous substance, deliquescent in air, soluble in water and alcohol, only slightly so in ether. It is dextro-rotatory, and reduces ammoniacal $AgNO_3$ with formation of a mirror.

The monobasic acid related to dulcitol is **lactonic acid**, which may be passed over here.

Mucic Acid, $COOH.(CHOH)_4COOH$, is the dibasic acid formed by the oxidation of dulcitol, milk-sugar, galactose, gums, etc. It is readily prepared by oxidising 1 part milk-sugar with a mixture of 2 parts HNO_3 sp. gr. 1·4 and 2 parts water. On evaporation mucic acid separates in crystals, which may be washed with water and dried. It forms white tables, m.p. 206°–216°, almost insoluble in cold water and alcohol. It does not reduce Fehling's solution.

CHAPTER XXXV.

HEXA-HYDRIC ALCOHOLS AND THEIR DERIVATIVES—Continued.

CARBOHYDRATES.

THE carbohydrates form a group of closely related substances which were originally given their name because in them the hydrogen and oxygen are present in the proportions necessary to form water.

They are divisible into the following groups :—

1. Saccharides, hexoses, or glucoses.
2. Disaccharides, or saccharoses.
3. Polysaccharides, which include the amyloses.

1. SACCHARIDES, HEXOSES, OR GLUCOSES.

The saccharides include such substances as dextrose and levulose, which are typical examples of the two classes into which these bodies are divisible, viz. the **Aldoses** and **Ketoses.** Aldoses are derived from a hexa-hydric alcohol by the oxidation of a *primary* alcoholic group, *e.g.* $CH_2(OH).(CHOH)_4.CH_2OH$ yields $CH_2(OH).(CHOH)_4CHO$. In ketoses, on the contrary, a *secondary* alcoholic group has been oxidised ; *e.g.* $CH_2(OH).(CHOH)_4CH_2OH$ gives $CH_2(OH).(CHOH)_3.CO.CH_2OH$.

ALDOSES.

Glucose, $C_6H_{12}O_6$ or $CH_2(OH).(CHOH)_4.CHO$, is considered to be the aldehyde of the alcohol sorbitol, and will be considered in some detail as illustrative of the aldehydes of the hexa-hydric alcohols. It occurs in three optically distinct forms. Of these—

d-**Glucose,** or **Dextrose,** *grape-sugar*, is the best known isomer. It is found in very many plant and animal substances, being widely distributed in the vegetable kingdom, where it occurs along with levulose and frequently with cane-sugar. Thus it is found in grapes and in most fruits, in honey, and in a combined state in many glucosides.[1] It is also present in the liver, in eggs, and in large quantities in the urine of those suffering from *diabetes mellitus.*

It has been recently synthetically produced from comparatively simple substances, but the processes are too complicated to detail here; suffice it to say that the starting-point is acroleïn (p. 210).

It is, however, readily formed by the hydrolysis of cane-sugar by invertase; and of sugar, starch, and cellulose by treatment with dilute acids. This latter process is commercially employed, and is known technically as "inversion." The equation in the case of sugar is—

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Levulose}}{C_6H_{12}O_6}$$

the mixed product being termed "invert sugar." The manufactured article goes under various names—glucose, saccharum, saccharine, and starch or corn sugar.

Manufacture.—Starches, rice, or maize are heated with solutions of H_2SO_4, HCl, or HNO_3, containing from 0·5 to 5 per cent. of pure acid. Either open or closed vessels are used; the latter, employed under pressure, are preferable because the time of "conversion" is then greatly decreased. The liquid obtained is neutralised, preferably by chalk, filtered from the calcium sulphate and other insoluble impurities, decolorised, usually by filtration through animal charcoal, and concentrated in vacuum pans, from which, when it contains 82 per cent. solid matter, it is run into moulds.

The impure glucose so obtained varies from white to brown in colour, according to the materials employed and the methods of manufacture. As impurities it may contain maltose, dextrin, and unfermentable substances, and may be further purified if requisite by adding crystals of anhydrous glucose to the concentrated syrup, and so inducing crystallisation, the product being separated from the syrup by means of a centrifugal machine; or it may be recrystallised from methyl alcohol.

Preparation of Pure Dextrose.—Pure dextrose may be

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[1] Glucosides are compound ethers which, when boiled with dilute acids, yield glucose (or some other sugar) and another body which is not a carbohydrate. Many occur in natural products.

prepared from a white commercial specimen by crystallising it first from alcohol, sp. gr. 0·82, then dissolving in 8–10 per cent. of water, and adding methyl alcohol to the solution till fine crystals of anhydrous glucose separate. Soxhlet recommends the following method for the preparation of a kilogram of glucose : mix 12 litres of alcohol, sp. gr. 0·81, with 480 c.c. strong HCl ; heat to 45°–50°, and stir in 4 kilos. powdered cane-sugar ; keep at this temperature for two hours ; then cool, and add a few crystals of anhydrous glucose and stir frequently. In about two days a large quantity of the sugar will separate. Wash it free from the mother liquor with alcohol till it is quite free from HCl, or recrystallise the precipitate from methyl alcohol.

Properties.—From aqueous solutions dextrose ordinarily separates in crystals with 1 molecule of water of crystallisation, $C_6H_{12}O_6, H_2O$, m.p. 86°; it can be obtained, however, from strong warm solutions, and also from methyl or ethyl alcohol in the anhydrous form, $C_6H_{12}O_6$, m.p. 146°. The hydrated form loses its water at 110°. Glucose is not so sweet as sugar, is readily soluble in water, but almost insoluble in absolute alcohol. When heated to 170°, it passes into a body called *glucosan* or *dextrosan*, $C_6H_{10}O_5$, which, on boiling with dilute acids, re-forms glucose. Sodium amalgam reduces dextrose in *alkaline* solutions to *mannitol.*

Strong HNO_3 oxidises it to saccharic acid, and eventually to oxalic and carbonic acids. It is easily attacked by alkalis, especially when hot, and reduces many oxides in alkaline solution either to a lower state of oxidation or to the metal. It is decomposed by the yeast ferment, yielding alcohol and CO_2 principally, but also smaller quantities of succinic acid and glycerol. Its solutions are dextro-rotatory (see p. 101). Its specific rotatory power[1] = $[a]_D = +52·7°$ for 10 per cent. solutions; freshly made solutions have almost double the rotatory power of old ones; on standing the normal rotation is slowly attained. Alkalis replace a hydrogen atom in dextrose, forming dextrosates, while such oxides as CaO and BaO, and salts like

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[1] For full explanation of the effect of sugar solutions on polarised light, a work on physics must be consulted. The determination of the specific rotation of a sugar solution in a "saccharimeter" enables us to determine its strength.

NaCl and NaBr combine molecularly with it to form well-defined compounds.

Identification.—The following tests aid in detecting the presence of dextrose: (1) It is not blackened by conc. H_2SO_4 (*difference from cane-sugar*). (2) It turns brown with alkalis. (3) If heated with NaOH, and then with *basic* bismuth nitrate, it readily yields a black precipitate. (4) It quickly reduces Fehling's solution[1] when heated, precipitating red Cu_2O. (5) It gives a mirror when gently warmed with an ammoniacal solution of $AgNO_3$ (the silver solution is best prepared by precipitating $AgNO_3$ by KOH, and just redissolving the precipitate in NH_4HO). (6) On heating glucose with a weak acetic acid solution of copper acetate, Cu_2O is precipitated (*dextrin, milk, cane or malt sugar do not give this except after long boiling*). (7) An aqueous solution of glucose boiled with NaOH gives a red colour (due to picramic acid) if a drop of picric acid solution is added.

Fructose, $CH_2(OH).(CHOH)_3.CO.CH_2OH$, is the ketonic alcohol derived from mannitol. It occurs in three forms; of these—

d-**Fructose** or **levulose,** *fruit-sugar*, occurs associated with grape-sugar in many fruits and in honey; and is readily produced (1) along with glucose in the hydrolysis of cane-sugar.

†*Process.*—Dissolve 100 grams of sugar in 1000 c.c. of water, add 20 c.c. of HCl, and carefully invert at 60°. Cool the solution to $-5°$, and add 60 grams of slaked lime (the temperature must be down to 2°); collect the lime compound, press, and wash two or three times with water. Suspend the precipitate in water, and decompose with oxalic acid or CO_2, filter, and concentrate; the levulose remains as a syrup.

If the syrup is repeatedly treated with cold absolute alcohol, this removes the water and other impurities. Keep the residue in a closed flask, when it will eventually crystallise; or, dissolve in hot alcohol, cool, separate from the syrupy levulose, which settles out, and allow the alcoholic filtrate to stand in a closed vessel, when it will deposit levulose in crystals.

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[1] Fehling's solution is prepared by dissolving 34·632 grams of $CuSO_4$, $5H_2O$, in 200 c.c. water, adding to that 173 grams of Rochelle salt in 480 c.c. of NaOH, sp. gr. 1·14, and diluting to 1 litre. 1 c.c. is reduced by 0·005 grams dextrose.

(2) Besides the method just given, since inulin (p. 276) is completely resolved into levulose on boiling with dilute acids, or on digestion for 20 hours with water at 100° C., it may be conveniently employed for preparing it; while (3) it is produced by the gentle oxidation of mannitol—

$$CH_2(OH).(CHOH)_4.CH_2OH + O$$
$$= CH_2(OH).(CHOH)_3.CO.CH_2OH + H_2O$$

Properties.—Levulose is generally found as a syrup, but yields silky needles (when prepared as described above), sp. gr. 1·6691, m.p. 95°.

When heated to 170° it loses a molecule of water, forming the anhydride *levulosan.* It is readily soluble in water, also in dilute alcohol; has a sweeter taste than dextrose, being as sweet as cane-sugar. Levulose is readily attacked by alkalis and by acids, and is easily reduced to mannitol by sodium amalgam in alkaline solution. Its oxidation products vary with the agent employed; it reduces Fehling's solution to the same extent as dextrose, but more slowly.

Levulose is lævo-rotatory; its specific rotatory power at 15° is $[a]_D = -98{\cdot}8°$: hence "invert sugar" is also lævo-rotatory, because the lævo-rotation of levulose is greater than the dextro-rotation due to dextrose.

The following reactions show the difference in behaviour between **dextrose** and **levulose.**

They both undergo fermentation with yeast, but the reaction is much slower in the case of levulose. Both compounds unite with HCN, and both with phenyl-hydrazine, the former with either one or two molecules of the reagent, the latter with two molecules, the *osazones* thus formed being identical.

They both show alcoholic characters; *e.g.* both give a penta-acetyl derivative when treated with acetic anhydride and $ZnCl_2$, and therefore both show the properties of penta-hydric alcohols; but dextrose readily yields on oxidation acids containing the same number of carbon atoms, while levulose is less easily oxidised, but gives acids containing less carbon than it. These results are in accordance with the assumption that dextrose is an aldehydic and levulose a ketonic alcohol, as shown by the formulæ given.

2. THE DISACCHARIDES OR SACCHAROSES.

These substances are ether-like anhydrides, derived from the saccharides by the elimination of water from two molecules of them. Sufficient is not known to enable us to decide definitely which groups interact in forming the new molecule, but the fermentable sugars are supposed to retain an aldehyde or ketone group intact. They undergo hydrolysis when warmed with dilute acids.

Cane-Sugar, $C_{12}H_{22}O_{11}$, **Saccharon,** or **Sucrose,** is very widely distributed in the vegetable kingdom. Considerable quantities are present in the juice of the sugar-cane (16 per cent.), in the sorghum, in the sap of palms, limes, and maples, especially the sugar maple, and in beet-root (7–14 per cent.) Besides these substances, it is found in moderate quantities in many fruits, generally accompanied by invert sugar. It is doubtful if it has been synthetically prepared.

Manufacture.—The manufacture of cane-sugar varies with the source of the sugar.

1. It is made from the sugar-cane by the following or some similar process :—

The juice, extracted from the ripe canes by crushing them, contains about 20 per cent. of sugar mixed with impurities. It is very liable to ferment, and is strained at once into the *clarifier*, where it is treated with sulphurous acid, then neutralised with lime and *defecated* by heating to 75°–80°, when a scum separates and is skimmed off. This treatment is repeated on the clarified liquid until it has a sufficient degree of consistency to be run into moulds, where it crystallises.

2. In making sugar from beet-roots, they are sliced, and then systematically lixiviated by warm water of gradually increasing temperature in a series of vessels termed *diffusers*, a strong solution finally being obtained. From 0·5 to 3·0 per cent. of lime is added to this liquid, which is boiled ; the clear juice is decanted into another vessel, where it is freed from excess of lime by passing in CO_2. The $CaCO_3$ formed is allowed to settle, and carries down with it other impurities. The above operations are repeated, and

the liquid, after filtering, is passed through animal charcoal or treated with SO_2 and filtered through sand to decolourise it. It is then evaporated down to sp. gr. 1·15 in vacuum pans, once more filtered through charcoal, and evaporated to the crystallising point.

The brown liquid remaining when the sugar crystallises out is termed *molasses*, or *treacle*, and contains a large quantity of sugar, which formerly was not recoverable. It is now recovered, amongst other ways, by forming strontium saccharosate, separating it, decomposing it by CO_2, and crystallising the sugar remaining.

Refining Sugar.—The raw sugar obtained by the two methods described, when required quite white as "lump" or "granulated" sugar, is dissolved in water, filtered, decolourised by filtration through charcoal, or by treatment with SO_2, and boiled down in a vacuum pan till crystallisable, the subsequent treatment depending on the form in which it is required.

Properties.—Pure cane-sugar is a transparent solid, which crystallises in monoclinic prisms. Its sp. gr. is 1·593 at $\frac{3\cdot 9^\circ}{}$. It is insoluble in ether, almost so in absolute alcohol, readily soluble in water, and also soluble in dilute alcohol in quantities which are not proportionate to the amount of water present, weak solutions dissolving more and strong ones less, than might be expected. Its solutions are dextro-rotatory $[a]_D$ at 20° being $+64\cdot 1$. It melts at 160°–161°, and does not crystallise again on cooling. If kept just above its melting point for some time it breaks up, forming dextrosan and levulosan; at 190°–200° it turns brown and then black, and forms **caramel** used for colouring purposes. If heated with water in closed tubes to 160° it is decomposed, CO_2, formic acid, and charcoal being formed. Boiling with water does not decompose it, but if a small quantity of some acid (especially mineral acids) is present, it is decomposed or "inverted" into an equi-molecular mixture of dextrose and levulose. This inversion takes place slowly in the cold, and CO_2 is sufficient to produce it.

Strong acids differ in their action; HNO_3 of 1·3 sp. gr. oxidises it with the production of saccharic, tartaric, and oxalic acids, while a mixture of strong HNO_3 and H_2SO_4 forms the explosive tetra-nitrate. Strong H_2SO_4 has only slow action on *dry* cane-sugar, but if added to a thick syrup rapid heating takes place, SO_2 is evolved, and a semi-solid carbonaceous mass results. Cane-sugar combines with bases, *e.g.* CaO, SrO, BaO, to form *saccharosates.*

Cane-sugar is *not* directly fermentable by yeast, but is hydrolysed by the enzyme invertase produced by it, and the invert sugar formed then ferments. It forms an octo-acetate when heated with sodium acetate and acetic anhydride, which proves the presence of eight hydroxyl groups in it, but its constitution is not yet established, though it is evidently an anhydride of dextrose and levulose.

Identification.—The following reactions are useful. A solution of cane-sugar does not turn brown when boiled with alkalis, nor give the smell of burnt sugar when afterwards acidified. Fehling's solution has no action in the cold, and on boiling for a minute or two the reduction is only slight (*difference from dextrose*). If, however, a solution of sugar is heated for a minute with a few drops of conc. HCl, and then neutralised with KOH, on addition of Fehling's solution dextrose may be detected. Ammoniacal silver nitrate solution is not reduced by heating with sugar solutions, but on addition of NaOH, a silver mirror is formed. The reaction with H_2SO_4 may also be noted.

Maltose, or **Malt-Sugar,** $C_{12}H_{22}O_{11}.H_2O$, *maltobiose,* is found in some glucoses and beers; it often occurs in the intestinal canal and in urine. Certain ferments which act on glycogen produce it, and it is yielded by the action of sulphuric acid upon starch. It is also formed, along with dextrin, from the starch present in grain, by the action of the ferment diastase—

$$3C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11} + C_6H_{10}O_5$$

Process.—Make 100 grams of starch into a paste with 2300 c.c. of water; cool down to 60° C., and mix with it 20 grams of air-dried malt, or the extract from that. Keep the mixture at 60°–65°, for four hours, cool, allow to stand for a few days, evaporate down *in vacuo,* and boil the residue with 2 litres of alcohol, sp. gr. 0·820. Decant the clear liquid, and put on one side for a week in a corked flask, when a crust of crystallised maltose will form on the side of the flask. The crystals may be purified by recrystallisation from either methyl or ethyl alcohol.

Properties.—Maltose crystallises in fine needles, sp. gr. 0·810, which become anhydrous at 100°. The anhydrous substance is little soluble in either methyl or in ethyl alcohol; the hydrated form is readily soluble both in them and in water. Its solution is dextro-rotatory, $[a]_D = +140°$ at 15·5°. Maltose undergoes no further change by the action of diastase, but is hydrolysed with formation of dextrose (compare Cane-sugar) by the pancreatic secretion, and by other ferments—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

It is also hydrolysed by dilute inorganic or organic acids, although not so readily as cane-sugar.

It is capable of direct fermentation by yeast. When boiled with HNO_3, it yields saccharic and oxalic acids; chlorine and bromine oxidise it to malto-bionic acid; heated with sodium acetate and acetic anhydride, it yields an octo-acetate. Malt sugar reduces Fehling's solution, but only to about two-thirds the extent of dextrose, and it *differs from that body* by being less soluble in alcohol, and not reducing a solution of $Cu\bar{A}_2$ made acid with acetic acid.

Maltose is evidently an anhydride of dextrose, and probably contains an unchanged aldehyde group.

Lactose, or **Milk-Sugar**, $C_{12}H_{22}O_{11}.H_2O$, *lactobiose*, is present to the extent of 5–8 per cent. in human milk, and in varying amounts in that of other mammals. It is also found in some other animal fluids, and is said to occur along with cane-sugar in the sap of a West Indian tree, *Achras sapota.* According to Demole, its octo-acetate can be synthesised by boiling a mixture of dextrose and galactose with acetic anhydride; this is, however, denied by other observers.

Manufacture.—Milk-sugar is prepared for commercial purposes by evaporating whey to dryness. The residue is dissolved in water along with a small quantity of alum, filtered through animal charcoal, evaporated to a syrup and crystallised. It may be purified by dissolving it in water, and reprecipitating it by the addition of alcohol.

Properties.—Lactose forms white, semi-transparent, rhombic crystals, sp. gr. 1·534 at 3·9°. It is less sweet and less soluble in water than cane-sugar. It is insoluble in alcohol and in ether. It crystallises (from water) with one molecule of water of crystallisation, which it loses if heated to 130°; at 180° it forms lacto-caramel, $C_{12}H_{20}O_{10}$, and above that it melts to a brown mass. Its solutions differ in rotatory properties according to their source; it is, however, dextro-rotatory, and normally $[a]_D = +52 \cdot 53$ at 20°. Pure yeast has no action upon it, although other organisms ferment it, producing alcohol and lactic acid. When heated with water to 170°, milk-sugar decomposes with separation of carbon, formic acid, and CO_2 (*vide* Cane-sugar, p. 269).

It turns brown when heated with alkalis, similarly to dextrose; organic acids have little effect, except when boiled with it, though oxalic acid does not act on it even at 100° (*difference from cane-sugar*); dilute mineral acids hydrolyse it, with formation of galactose and dextrose. Concentrated H_2SO_4 has no action upon milk-sugar till heated with it. Dilute HNO_3 oxidises it to mucic and saccharic acids; concentrated HNO_3 forms nitrates. Lactose prevents the precipitation of metallic oxides by means of caustic alkalis, readily reduces Fehling's solution, yields a silver mirror with ammoniacal silver solutions, but does not reduce Barfoed's solution $(Cu\bar{A}_2 + H\bar{A})$. If it is boiled with a solution of lead acetate, and AmHO is then added, a precipitate is obtained which is first yellow and then copper red.

Lactose forms, like the other sugars, an octo-acetate, and by several of its reactions may be shown to be an anhydride of galactose and dextrose, in which the aldehyde group of the dextrose remains intact.

CHAPTER XXXVI.

CARBOHYDRATES—Continued.

3. THE POLYSACCHARIDES.

MUCH less is known about the constitution of these substances than of the other saccharides. As far as we know, their constitution is very complex, and their molecular weight great.

Starch, $(C_6H_{10}O_5)_n$, where n is probably 100 at least, *amylum*, occurs in varying quantities in many different parts of plants, such as the leaves, stems, flowers, fruit, and roots. It is formed in the chlorophyll cells—sugars probably being first formed—and it serves as a reserve food for the plant. Starches, such as sago, tapioca, and those in grain, are important as food for men and animals. The following numbers show the approximate amounts present in different substances: wheat, 55; barley, 45; rice, 75; peas and lentils, 39; potatoes, 16–23; yams, 25 parts starch per cent.

Manufacture.—The principal substances used in the manufacture of starch are wheat, maize, rice, and potatoes; and the following is a short description of the processes employed:—

In the simplest and oldest method, the grain is softened by soaking, next crushed, and the starch then washed out by frequent treatment with water. The milky liquid, which contains the starch along with a quantity of gluten, is allowed to stand until the latter is destroyed by fermentation. The supernatant liquid is then drawn off, and the starch washed by frequent stirring up with water, allowing the mixture to settle, and drawing off the wash-water.

In another method flour is employed; this is made into dough, is then washed on sieves and in centrifugal machines till free from starch, which is purified by washing with weak caustic soda, and then with water till free from alkali.

To prepare starch from potatoes, these are ground to pulp and then washed in centrifugal machines or on sieves, with water made acid with H_2SO_4. The starch so obtained is purified similarly to that just described.

Experiment 16.—Make 100 grams of flour into a stiff paste, wrap it in a piece of calico and knead it in water. Notice that the water becomes milky in appearance, and, if allowed to stand, deposits a white sediment, while the gluten remains behind in the calico. Boil part of the sediment with a little water, and apply the tests for starch given below. Also examine some of it with a microscope, using a $\frac{1}{6}$-inch objective. The granules obtained by cutting a slice off a potato and smearing a microscope slide with it may also be examined.

Properties.—Starch is a white lustrous powder, sp. gr. dry varying from 1·56 to 1·65, and, with the exception of that from potatoes, is without taste or smell. This powder consists of minute granules (Fig. 45).

The granules from different sources differ characteristically in appearance and size. They each consist of a nucleus or hilum, surrounded by concentric layers, which are made visible by treatment with dilute alkali. They have the power of polarising light, and so yield characteristic effects when examined by polarised light. The largest granules are those from *tous les mois* or potatoes, 0·175 mm. and 0·140 mm. in diameter respectively; the smallest are from beet-root starch, 0·0004 mm. in diameter.

If the granules are entire, starch is insoluble in cold water, but when treated with boiling water the granules swell and burst; the cell-walls (starch cellulose or *farinose*) remain insoluble, while the cell-contents (*granulose*) go into solution. Air-dried starch contains 18–20 per cent. of moisture, and, if carefully dried, may be heated to 160° without change; at a higher temperature it undergoes change, with partial formation of dextrin. If starch paste is boiled with dilute alkalis, or if starch is heated to 190° with glycerol, "soluble" starch is produced.

Boiling dilute acids convert starch into dextrin and maltose, and finally dextrose. Strong HNO_3 forms first saccharic acid, and then oxalic acid; while fuming HNO_3 mixed with conc. H_2SO_4 nitrates it. Many unorganised ferments (enzymes) possess the power of liquefying starch; the action of diastase is note-worthy (see Dextrin, p. 276).

Identification.—Iodine gives, with moist starch or cold starch

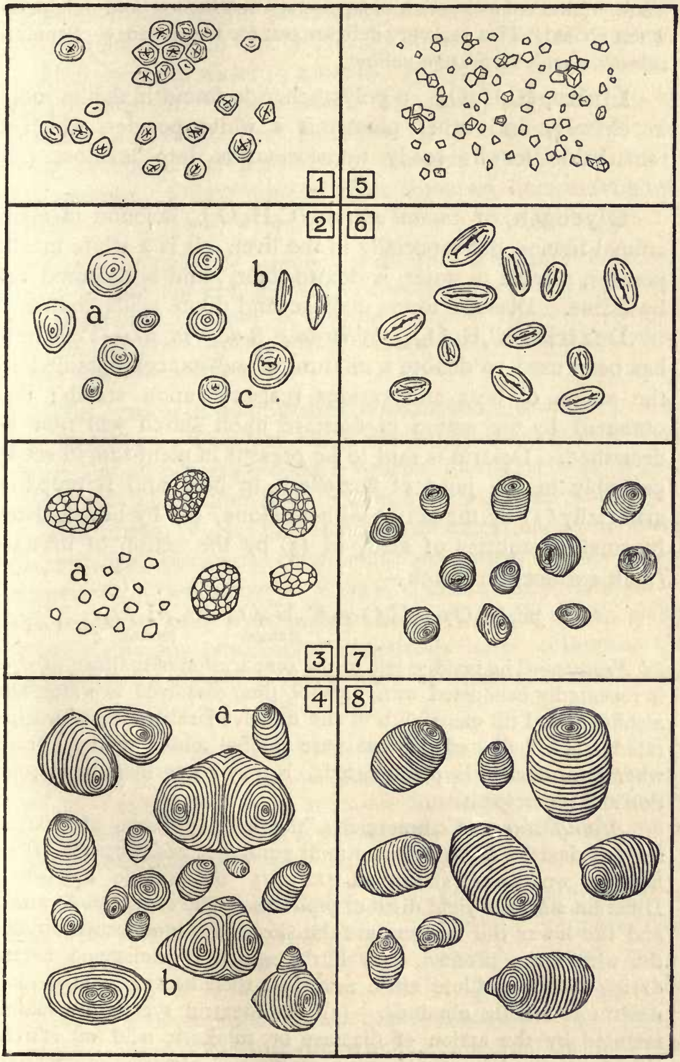

Fig. 45.—1. Maize. 2. Wheat: (b) side view; (c) cracked from desiccation. 3. Oat: compound grains and (a) single granules. 4. Potato: (a) hilum; (b) compound granule. 5. Rice. 6. Bean. 7. West Indian arrowroot. 8. Tous les mois.

paste, a blue colour, which disappears when heated and reappears when cooled. This is a very delicate test for its presence. Bromine colours starch an orange-yellow.

Inulin, $(C_6H_{10}O_5)_n$, a polysaccharide found in dahlia roots, in chicory, and other plants, is a white powder, which is remarkable for its ready transformation into levulose (see p. 267).

Glycogen, or *animal starch*, $(C_6H_{10}O_5)_n$, is found in many animal tissues, but especially in the liver. It is a white meally powder, soluble in water, is dextro-rotary, and is coloured red by iodine. Diastase forms maltose, and dilute acids dextrose.

Dextrin, $(C_6H_{10}O_5)_n$, *Sullivan's β-dextrin iii.*—This term has been used to denote a mixture of substances obtained by the action of heat and various reagents upon starch; that obtained by the action of diastase upon starch will now be described. Dextrin is said to be present in plant-sap, in seeds, probably in the juice of horseflesh, in beer, and is prepared artificially (1) by the action of heat alone, (2) by heat assisted by small quantities of acid, or (3) by the action of diastase (malt extract) on starch—

$$3C_6H_{10}O_5 + H_2O = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{C_6H_{10}O_5}$$

Process.—The residue left in the preparation of maltose (p. 270) is repeatedly exhausted with alcohol, then dissolved in water, and alcohol added till one-eighth of the dissolved substance is precipitated; this is filtered off, and pure alcohol added to the filtrate, when pure dextrin is precipitated. It may be purified by re-solution and reprecipitation.

Manufacture.—Commercially, the various forms of dextrin, such as dextrin, British gum, starch gum, etc., are prepared (1) by heating well-dried starch to 212°–275° in suitable apparatus. Different starches yield distinct products at the same temperature, and the lower the temperature the slower the transformation, but the whiter the product. (2) If the starch is moistened before drying with very dilute nitric acid, and then heated to 110°–120°, dextrin is readily obtained. (3) The dextrin syrups are manufactured by the action of diastase or sulphuric acid on starch. When prepared by the former, maltose is always present, and dextrose in the latter case. These dextrins are employed as gum substitutes and in the manufacture of beer.

Properties.—Dextrin is an uncrystallisable, glassy, colourless substance, which can be rubbed down to a white powder.

It dissolves in water to a neutral syrup, from which alcohol reprecipitates it. Its solutions are dextro-rotatory $[a]_D = +200{\cdot}4$ for a 10 per cent. solution. It is not fermentable by yeast, except in the presence of diastase, which converts it into maltose. Dilute mineral acids act upon dextrin as upon starch.

Identification.—The reactions of dextrin are not very characteristic. It does not reduce Fehling's solution, or only slightly so, and is precipitated from its aqueous solutions by the addition of alcohol (*difference from dextrose*). It is not coloured by iodine (*difference from starch*).

The **isomeric** or **polymeric dextrins** are similar to that just described. They are white substances readily soluble in water, and all possess the same specific rotatory power $[A]_D = +200{\cdot}4$. They differ from dextrin by being fermentable.

Cellulose, $(C_6H_{10}O_5)_n$, or some modification of it, forms the principal portion of most plant structures. In its purest natural form we know it as raw cotton, which consists of the vegetable hairs surrounding the seeds of the cotton plant. This yields on purification practically pure cellulose, the only impurity present being a trace of mineral matter, which leaves 0·1 to 0·2 per cent. of ash.

Process of Purification.—Treat cotton wool frequently in alternation with cold bromine water (bromine has no action on cellulose) and boiling dilute ammonia till nothing more is removed by the alkali. Then wash it successively with dilute acid, water, alcohol, and ether, and dry.

Properties.—Pure cellulose is a white semi-transparent colloidal substance, of sp. gr. 1·45. It usually contains about 7 per cent. of moisture, which is, however, probably water of hydration. It is insoluble in all ordinary solvents, but it dissolves in cuprammonia (Schweitzer's reagent),[1] from which it may be reprecipitated by dilute acid. The soluble compound

---

[1] This may be prepared by dissolving well-washed copper hydrate in the least possible quantity of strong ammonia.

produced is said to be $(C_6H_{10}O_5)_2.Cu(NH_4)_2O$. It is also soluble in a hydrochloric acid solution of zinc chloride, of sp. gr. 1·44. Dilute potash or soda have little or no action upon it, but if concentrated they profoundly modify the structure of the fibre, forming $C_{12}H_{20}O_{10}.Na_2O$. Dilute acids have little action at ordinary temperatures, but destroy it on heating. Strong H_2SO_4 dissolves cellulose with the formation of acid sulphates.

Strong HNO_3, either alone or with conc. H_2SO_4, forms nitrates (see Nitro-cellulose, below). Cellulose is slowly disintegrated by H_2SO_4 of 1·35 sp. gr., or HNO_3 of 1·3, but a toughening first occurs. This reaction is employed to form parchment paper, and may be shown as follows—

Experiment 17.—Pass strips of filter-paper *rapidly* through a mixture of 3 parts strong H_2SO_4, and 1 part water; wash at once in dilute ammonia, and then in water, and note the increased strength of the paper.

Moist chlorine oxidises cellulose, bromine has no effect upon it, and iodine gives no colour; but hypochlorites attack it, producing oxycellulose, which is remarkable for its affinity for vanadium compounds.

Identification.—Though cellulose gives no reaction with iodine alone, after treatment with a dehydrating agent a blue colour is obtained. A useful reagent is a mixture of 90 parts of $ZnCl_2$ solution, sp. gr. 2, 6 parts of KI, and 10 parts of water, with a little iodine dissolved in it; this gives a blue colour when applied to cotton or other form of cellulose. Or cotton may be rubbed with a mixture of 3 parts strong H_2SO_4, 2 parts glycerol, and 1 part water. If a drop of dilute iodine solution is then applied, the blue colour is obtained.

Cellulose Nitrates, *nitro-celluloses* or *pyroxylines.*—Cellulose contains hydroxyl groups, and when treated with strong nitric acid, under suitable conditions, nitrates are easily formed. These contain a varying number of (NO_3) groups according to the conditions of the experiment. Of these, the hexa-nitrate forms **gun-cotton**, and the tri- and tetra-nitrates are used for making **collodion.** These nitrates have certain common properties: many reducing agents reconvert them into cellulose ; alkaline solutions remove the nitric acid radicle, *i.e.* they are saponified ; on boiling with HCl and $FeSO_4$ their nitrogen is given up as nitric acid ; and all are more or less explosive.

Gun-cotton, $C_{12}H_{14}(NO_3)_6O_4$, is prepared by treating cotton with a mixture of 3 parts HNO_3, sp. gr. 1·5, and 1 part H_2SO_4, sp. gr. 1·84, for twenty-four hours. The temperature must not exceed 10°, and the product is afterwards thoroughly washed free from acid. This body is insoluble in alcohol or in ether, or in a mixture of them, and slowly soluble in acetone. It is hardly distinguishable from cotton in appearance, gives no blue colour with iodine, and is insoluble in cuprammonia. It burns quietly when ignited, but explodes violently by percussion, especially if compressed. It is not affected by water, and therefore can be stored in a *wet* condition, and is quite safe if thoroughly free from acid.

Collodion is composed of a mixture of tri- and tetranitrates, prepared by nitrating cellulose at a higher temperature and with weaker acids, and differs from gun-cotton by being soluble in ether-alcohol.

APPENDICES

1. Calculation of Percentage Composition. *Extra Example.*—0·3636 gram of caffeine yielded 0·6601 gram of CO_2 and 0·171 gram of water; also 0·1283 gram yielded, when analysed by Will and Varrentrap's process (p. 19), 0·2613 gram of platinum.

The percentage amount of carbon present (see p. 24), is—

$$0·6601 \times \frac{3}{11} \times \frac{100}{0·3636} = 49·50$$

The percentage amount of hydrogen present (p. 24), is—

$$0·171 \times \frac{1}{9} \times \frac{100}{0·3636} = 5·22$$

Since in the formula of $(NH_4)_2PtCl_6$ one atom of carbon corresponds to two atoms of nitrogen—

195 grams Pt correspond to 28 grams N

$\therefore$ 1 gram Pt corresponds to $\frac{28}{195}$ gram N

and 0·2613 „ Pt „ to $\frac{28}{195} \times 0·2613$ gram N

But that amount of nitrogen was present in 0·1283 gram caffeine; the percentage amount present will therefore be—

$$\frac{28}{195} \times 0·2613 \times \frac{100}{0·1283} = 29·44$$

The percentage amount of oxygen will be, by difference, 16·04.

2. Aceto-acetic Ester, or Ethyl Aceto-acetate, and its Derivatives.—These compounds have proved very important in the synthesis of fatty acids and ketones. The methods of their preparation, and their decompositions, will accordingly be described.

To prepare ethyl aceto-acetate the following process may be used: 1000 grams of carefully dried ethyl acetate are treated with 100 grams of sodium in small pieces, and after the first reaction is over the mixture is heated, in a flask with a reflux condenser attached, till the sodium is dissolved. 550 grams of 50 per cent. acetic acid are added, and, when the mixture is cool, 500 c.c. of water. The oily layer that separates is washed with water and fractionated, and about 175 grams of a liquid boiling at about 180° may eventually be obtained. The reactions may be thus represented—

$$2CH_3.COO(C_2H_5) + Na_2 = \underset{\text{Sodio-aceto-acetic ester}}{CH_3.CO.CHNa.COO(C_2H_5)} \\ + C_2H_5ONa + H_2$$

$$CH_3.CO.CHNa.COO(C_2H_5) + CH_3.COOH = \\ \underset{\text{Aceto-acetic ester}}{CH_3.CO.CH_2.COO(C_2H_5)} + CH_3.COONa$$

The ester is a neutral liquid with a fragrant odour, b.p. 181°, slightly soluble in water, readily in alcohol. It yields a violet-red colour if $FeCl_3$ is added to its aqueous solution. If it is decomposed by *cold* KOH it is saponified, and free aceto-acetic acid can be obtained by acidification with dilute acids and extraction with ether. If the ester is dissolved in absolute alcohol, and an equivalent amount of sodium added, hydrogen is liberated, and the sodio-derivative is formed; if to this solution an alkyl iodide is added and heat applied, the sodium is replaced by the alkyl group. If the treatment with sodium alcoholate and the iodide is repeated, a second hydrogen atom can be displaced. Thus, according as one or two hydrogen atoms are replaced, compounds of the following types are formed:—

$$CH_3.CO.CH(CH_3).COO(C_2H_5) \text{ and } CH_3.CO.C(CH_3)_2.COO(C_2H_5)$$

in which the methyl group may be replaced by other similar radicles.

Free aceto-acetic acid breaks up readily, when heated, into acetone and CO_2—

$$CH_3.CO.CH_2.COOH = CH_3.CO.CH_3 + CO_2$$

The esters and their alkyl derivatives may be broken up in two ways, yielding ketones and acids as the respective results.

If they are heated with *dilute* KOH, or if they are boiled with H_2SO_4, or with HCl (1 part acid to 2 parts water), CO_2 is split off and **ketones** are formed; *e.g.*—

$$CH_3.CO.CH_2 \vdots COO(C_2H_5) + 2KOH = CH_3.CO.CH_3 + K_2CO_3 \\ + C_2H_5OH$$

$$CH_3.CO.CH(C_2H_5) \vdots COOC_2H_5 + 2KOH = CH_3.CO.CH_2.C_2H_5 \\ + K_2CO_3 + C_2H_5OH$$

If *concentrated* alcoholic KOH is employed, the reaction differs, acids being produced ; *e.g.*—

$$CH_3.CO.\vdots CH_2.COO(C_2H_5) + 2KOH = CH_3.COOK + CH_3COOK + C_2H_5OH$$

$$CH_3.CO.\vdots C(CH_3)_2.COOC_2H_5 + 2KOH = CH_3.COOK + CH(CH_3)_2.COOK + C_2H_5OH$$

The cleavage of the molecule occurs as indicated by the dotted lines. It will thus be recognised that these reactions furnish us with valuable means of readily synthesising from ethyl aceto-acetate either fatty ketones or fatty acids, whose compositions will vary according to the alkyl groups introduced.

If the sodium compounds are treated with halogen derivatives of esters, then acid derivatives are obtained which decompose similarly to the alkyl compounds, but yield acids of the succinic series.

Thus monochlor-acetic ester $CH_2Cl.COO(C_2H_5)$ produces $CH_3.CO.CH(CH_2.COOC_2H_5).COOC_2H_5$ which breaks up and gives succinic acid—

$$CH_3.CO.\vdots CH(CH_2.COOC_2H_5).COOC_2H_5 + 3H_2O = CH_3.COOH + C_2H_4(COOH)_2 + 2C_2H_5OH$$

3. Ethyl Malonate, or **Malonic Ester,** $CH_2(COOC_2H_5)_2$, can be prepared by passing HCl gas into a solution of cyanacetic acid in absolute alcohol, or by the following process :—

Dissolve 125 grams of chloracetic acid in 250 c.c. of water and 93·5 grams of K_2CO_3 ; add 87·5 grams of KCN, and heat to start the reaction. As soon as the action is over, evaporate the liquid down over a sand-bath till its temperature is 135°. Then cool, add the mass to two-thirds its weight of absolute alcohol, and pass in HCl. Pour the product into ice-water, extract with ether, dry over $CaCl_2$, and distil.

It is a liquid with a faintly aromatic odour, b.p. 195°. It resembles ethyl aceto-acetate in containing a CH_2 group, the hydrogen of which can be replaced successively by sodium and by alkyl radicles, thus yielding substituted malonic esters. From these the free acids can be obtained, and as they (like malonic acid itself) lose, when heated, a molecule of CO_2 and yield fatty acids, we have another method of synthesising higher fatty acids.

Thus $C(C_2H_5)_2(COOC_2H_5)_2$ yields $C(C_2H_5)_2(COOH)_2$, which in turn gives on heating $CH.(C_2H_5)_2COOH + CO_2$.

4. Oxidising Agents.—The following are some of the principal substances employed in oxidising organic compounds.

1. There are cases in which free **oxygen** acts upon readily oxidisable substances, especially in presence of spongy platinum; thus alcohol can be oxidised to aldehyde, and then to acetic acid.

2. **Chromic Acid** itself, or a mixture of $K_2Cr_2O_7$ along with either H_2SO_4 or acetic acid, is often employed. For the oxidation of alcohols a solution of 3 parts $K_2Cr_2O_7$, 1 part H_2SO_4, and 10 parts water is useful; for hydrocarbons stronger solutions may be employed. One molecule of the salt yields three atoms of oxygen, and the equation may be represented as—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

3. **Nitric Acid,** sp. gr. 1·4, diluted with 2 volumes of water may frequently be employed, the amount of oxygen yielded being dependent upon the conditions of the experiment. It is also employed in the concentrated form.

4. **Potassium Permanganate** is used both in alkaline and in acid solution. In the first case two molecules of the salt yield three atoms of oxygen; in the second they give five atoms—

$$2KMnO_4 + 3H_2O = 2Mn(OH)_2 + 2KOH + 3O$$
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO4 + 3H_2O + 5O$$

The action of the H_2SO_4 upon the oxide of manganese explains the increased amount of oxygen in the second case.

Manganese Dioxide (or, at a higher temperature, lead dioxide) can be employed along with H_2SO_4—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

5. **Chlorine** and **bromine** both act as oxidising agents in presence of water—

$$Cl_2 + H_2O = 2HCl + O$$

6. **Silver Oxide** is also employed for oxidising aldehydes (see Formation of acrylic acid), while

7. **Potassium Ferricyanide** in alkaline solution is a mild oxidising agent—

$$2K_3FeCy_6 + 2KOH = 2K_4FeCy_6 + H_2O + O$$

5. Reducing Agents.—1. At a high temperature **hydriodic acid** acts as a powerful reducing agent, and is frequently employed to reduce polyhydric alcohols; when a large excess is used, it is possible to reduce acids to hydrocarbons.

2. **Sodium**, either alone or as **sodium amalgam,** when acting

in alcoholic or in moist ethereal solution, is a very powerful reagent—

$$Na_2 + 2H_2O = 2NaOH + H_2$$

3. **Zinc** may be used either in acid or in alkaline solution—

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Zn + 2KOH = Zn(OK)_2 + H_2$$

Zinc dust (a mixture of Zn and $Zn(OH)_2$) is frequently employed. Difficultly reducible substances are often heated to a high temperature with zinc dust alone.

4. **Iron** and **tin** are also employed along with acids, and it should be noted that the $FeCl_2$ and the $SnCl_2$ formed from these metals and HCl are themselves reducing agents. In presence of readily reducible substances, $SnCl_2$ reacts as follows:—

$$SnCl_2 + 2HCl = SnCl_4 + H_2$$

Besides the above-mentioned reagents, 5. **Sulphuretted hydrogen** finds some employment in ammoniacal solution; and 6. **Sulphur dioxide** in aqueous solution.

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The figures in black type indicate the principal reference, where more than one is given.

THE END.

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